Environmental Technology Verification Report

ISOTOPIC CARBON DIOXIDE ANALYZERS
FOR CARBON SEQUESTRATION MONITORING
PICARRO CAVITY RING-DOWN SPECTROSCOPY
ANALYZER FOR ISOTOPIC CO_2 - MODEL G1101-i

Prepared by
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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

ISOTOPIC CARBON DIOXIDE ANALYZERS FOR CARBON SEQUESTRATION MONITORING PICARRO CAVITY RING-DOWN SPECTROSCOPY ANALYZER FOR ISOTOPIC CO_2 - MODEL G1101-*i*

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Foreword

The EPA is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of six environmental technology centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. Under a cooperative agreement, Battelle has received EPA funding to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

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List of Abbreviations

%D	percent difference	QMP	Quality Management Plan	
%R	percent recovery	RMO	Records Management Office	
%RSD	percent relative standard deviation	$\delta^{13}C$	relative difference in stable carbon isotope ratio from PDB standard	
ABT	ambient breeze tunnel			
ADQ	audit of data quality	RPD	relative percent difference	
AMS	Advanced Monitoring Systems	SIL	Stable Isotope Lab	
		sccm	standard cubic centimeters per minute	
CCL	Central Calibration Laboratory			
		s	standard deviation (n-1)	
cfm	cubic feet per minute	σ	standard deviation (n)	
CO_2	carbon dioxide	TQAP	test/quality assurance plan	
CRDS	cavity ring-down spectroscopy	TSA	technical systems audit	
		WMO	World Meteorological Organization	
DFB	distributed feedback			
DQIs	data quality indicators			
EPA	U.S. Environmental Protection Agency			
ETV	Environmental Technology Verification			
GS	geologic sequestration			
GHz	gigahertz			
Hz	hertz			
INSTAAR	Institute for Arctic and Alpine Research			
IRMS	isotope ratio mass spectrometry			
ISO	International Organization for Standardization			
LPM	liter per minute			
LRB	laboratory record book			
MHz	megahertz			
m	meters			
m/s	meters per second			
NDIR	nondispersive infrared			
NOAA	National Oceanic and Atmospheric Administration			
ppm	parts per million (mole fraction)			
PDB	Pee Dee Belemnite			
PE	performance evaluation			
‰	per mil (part per thousand)			
PO	project officer			
QA	quality assurance			
QC	quality control			
QCL	quantum cascade laser			

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible. The definition of ETV verification is to establish or prove the truth of the performance of a technology under specific, pre-determined criteria or protocols and a strong quality management system. The high quality data are assured through implementation of the ETV Quality Management Plan. ETV does not endorse, certify, or approve technologies.

The EPA's National Risk Management Research Laboratory (NRMRL) and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of the Picarro Cavity Ring-Down Spectroscopy Analyzer for Isotopic Carbon Dioxide (CO_2) - Model G1101-*i*.

Chapter 2
Technology Description

This report provides results for the verification testing of the Picarro, Inc., Model G1101-*i*. The following is a description of the Model G1101-*i* carbon dioxide isotope analyzer based on information provided by the vendor. The information provided below was not verified in this test.

The Model G1101-*i*, shown in Figure 1, is a low-drift, high precision analyzer designed to measure the stable isotope ratio of carbon ($\delta^{13}C$) in carbon dioxide (CO_2). This analyzer is based on cavity ring-down spectroscopy (CRDS), which is a technique in which a gas sample is introduced into a high finesse optical cavity and the optical absorbance of the sample is determined, thus providing concentration or isotopic ratio measurements of a particular gas species of interest[1,2].

Figure 1. The Picarro Model G1101-*i* carbon dioxide isotope analyzer

Figure 2 shows a block diagram of the Picarro CRDS analyzer. The components which make up a basic CRDS instrument are a laser, a high finesse optical cavity consisting of two or more mirrors, and a photo-detector. Operationally, light from a laser is injected into the cavity through one partially reflecting mirror. The light intensity inside the cavity then builds up over time and is monitored through a second partially reflecting mirror using a photo-detector located outside the cavity. The "ring-down" measurement is made by rapidly turning off the laser and measuring the light intensity in the cavity as it decays exponentially with a time constant, τ, that depends on the losses due to the cavity mirrors and the absorption and scattering of the sample being measured. After shutting off the laser, most of the light remains trapped within the cavity for a relatively long period of time (i.e., microseconds [μsec]), producing an effective path length of tens of kilometers through the sample. Much like a multi-pass cell, this long effective path length gives CRDS its high sensitivity.
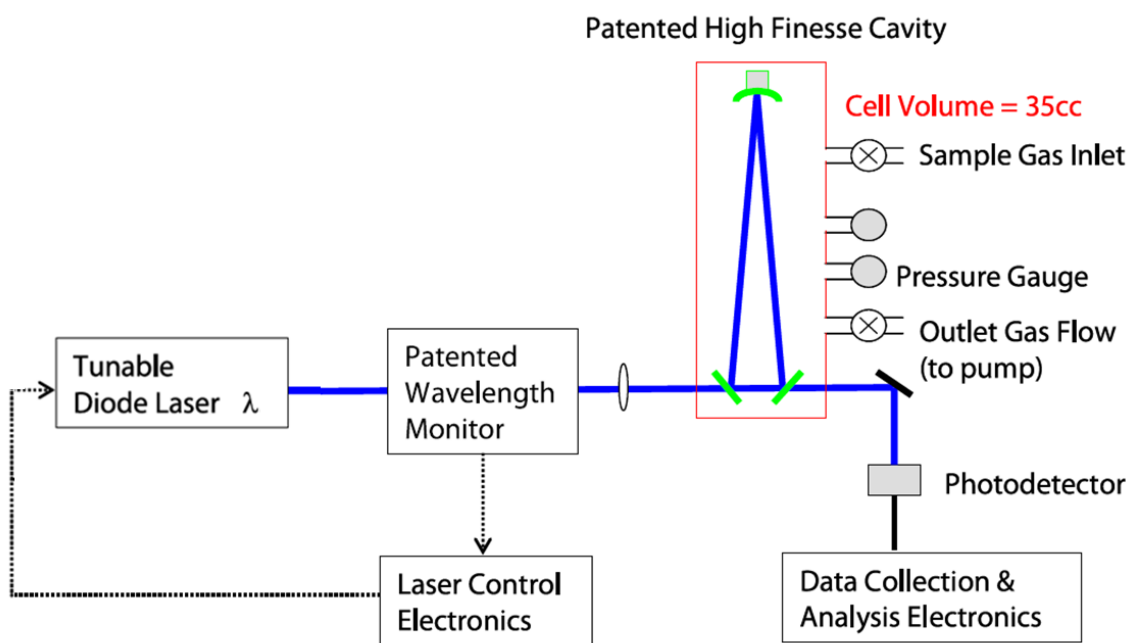
Figure 2. Block diagram of the Picarro Model G1101-*i* carbon dioxide isotope analyzer

The Model G1101-*i* utilizes a telecom-grade distributed feedback (DFB) laser. Light from the DFB laser is transported to a wavelength monitor via a polarization maintaining optical fiber. The analyzer is designed to simultaneously measure optical absorption using a proprietary traveling wave cavity and the optical frequency at which the absorption occurs using a proprietary wavelength monitor. The temperature and pressure of the ambient air sample continuously flowing through the optical cavity are regulated at all times. A typical empty cavity decay constant, τ, is 40 μsec for this instrument. The normalized reproducibility of the measured ring-down time constant ($\Delta\tau/\tau$) is better than 0.02%. With a ring-down acquisition rate of 100 hertz (Hz), the typical sensitivity of the instrument is $1.6\times10^{-11}\text{cm}^{-1}/\text{Hz}^{1/2}$.

The analyzer continuously scans the laser over two individual CO_2 rovibrational (i.e., rotational and vibrational excitation of the CO_2 molecule) resonant absorption lines, one for $^{12}CO_2$ and one for $^{13}CO_2$. Each spectrum is comprised of absorption loss as a function of optical frequency. The

concentration is proportional to the area under each measured spectral feature. Concentration measurements are provided approximately every second, corresponding to a total of 100 ring-down and wavelength monitor measurements, and the isotope ratio is derived from the ratio of the concentrations.

The wavelength monitor used in the analyzer is solid-state in design and has no moving parts. It is designed to provide wavelength measurements over a frequency range corresponding to greater than 100 nm. The wavelength precision (defined as the repeatability of the wavelength measurement at a single spectral point and calculated as one standard deviation (σ)) is approximately 1 MHz (1σ). The relative accuracy, defined as the repeatability of the difference of the wavelength measurement between two spectral points separated by approximately 1 GHz (the width of a typical absorption line at a typical operating pressure of 140 Torr) during a spectral scan is designed to be approximately 0.3 MHz. The size and shape of the CO_2 spectral lines are sensitive to temperature and pressure of the sample, but typically are 6250 wavenumbers (i.e., wave property proportional to the reciprocal of the wavelength). Therefore, the analyzer is designed to control the sample gas temperature to a precision (1σ) of a few hundredths of a K over ambient temperatures ranging from 10 to 35ºC and the sample pressure to a precision (1σ) of 0.05 Torr. In the analyzer, a combination of proportional valves (for flow control) is used to maintain the cavity at a known constant pressure.

The Model G1101-*i* weighs 26.3 kg (58 lbs), has dimensions of $43 \times 25 \times 59$ cm (17" $\times$ 9.75" $\times$ 23") including the feet, and can be rack mounted or operated on a benchtop. The approximate purchase price of the Model G1101-*i* is US $60,500.

Chapter 3
Test Design and Procedures

3.1 Test Overview

This verification test was conducted according to procedures specified in the *Test/QA Plan for Verification of Isotopic Carbon Dioxide Analyzers for Carbon Sequestration Monitoring*[3] (TQAP) and adhered to the quality system defined in the ETV AMS Center Quality Management Plan (QMP)[4]. As indicated in the test/QA plan, the testing conducted satisfied EPA QA Category III requirements. The test/QA plan and/or this verification report were reviewed by:

- Chuck Dene, Electric Power Research Institute
- Sam Krevor, Stanford University
- Eben Thoma, U.S. EPA
- Dominic DiGiulio, U.S. EPA
- Bruce Kobelski, U.S. EPA.

Battelle conducted this verification test with funding support from the EPA's Forum for Environmental Monitoring and with in-kind support from the National Oceanic and Atmospheric Administration (NOAA).

Research on carbon storage in geologic reservoirs such as saline formations, coal seams, and depleted oil and gas fields, has gained momentum in recent years as interest in mitigation of greenhouse gases, such as CO_2, has increased and a number of pilot-studies have recently been brought online. Capture and geologic sequestration (GS) of CO_2 involves capturing emissions at a power plant or other large source, separating the emissions to isolate CO_2, and compressing the gas. The compressed CO_2 is injected into a deep underground rock formation. Potential sites are carefully evaluated for adequacy of containment layers, seismic stability, and other factors. As pilot and full-scale geologic sequestration programs continue to be implemented, so do the needs to monitor leakage.

Stable isotope analysis can be used in environmental forensics, for example to aid in determining the source of carbon dioxide. Deviations in the ratio of ^{13}C to ^{12}C ($^{13}C/^{12}C$) in atmospheric CO_2 relative to that in ambient air can be used to identify input from other carbon sources, such as fossil fuel combustion, since atmospheric, carbonate, and plant-derived carbon differ in their $^{13}C/^{12}C$ relative to the Pee Dee Belemnite (PDB) standard. The relative difference in stable carbon isotope from the PDB standard, referred to as $\delta^{13}C$, is calculated as shown in Equation 1 and expressed in per mil (‰), or part per thousand.

$$\delta^{13}C_{Sample} = \left(\frac{^{13}C/^{12}C_{Sample}}{^{13}C/^{12}C_{PDB}} - 1 \right) \times 1000 \qquad (1)$$

Since the PDB standard was highly enriched in ^{13}C, most naturally occurring carbon sources have a negative δ^{13}C value. For example, ambient air CO_2 has a global average δ^{13}C close to −8‰ (cf., ref 5) and the global mean value from a 1991 inventory of fossil fuel types was −28.5‰.[6,7] Stable isotope measurements are traditionally conducted on discrete samples, such as air collected in canisters, in the laboratory using isotope ratio mass spectrometry (IRMS), but recent advances in spectroscopic monitoring technology have made it possible to conduct in situ measurements of stable isotope ratios with high frequency and precision.[8,9]

The use of isotopic CO_2 analyzers for ambient air monitoring in areas near GS sites, for example, could be used to identify intrusion of non-ambient CO_2 and provide information about its source. Large-scale leaks in high risk areas where the source is well-understood can be detected by conventional CO_2 analyzers. Fast-response, portable analyzers, including infrared "cameras," could be useful as a survey tool to quickly assess larger geographic areas for large-scale leaks. The high sensitivity and fast response of isotopic CO_2 analyzers have the potential to detect smaller leaks and identify larger subsurface leaks before exceeding the detection limits of less sensitive techniques. Spectroscopic isotopic CO_2 analyzers have been proposed as a potentially viable technology for monitoring GCS sites, nearby communities, and sensitive ecosystems for CO_2 leaks, where analyzers would need to have sufficient accuracy and precision to detect background ambient air concentrations (~350 ppm) and δ^{13}C values (~ −8‰) and capture daily/seasonal variability.

This verification test evaluated the performance of the Model G1101-*i* while conducting measurements of CO_2 concentration and δ^{13}C in synthetic gas mixtures and in ambient air. One of the goals of this verification test was to provide information on the potential use of the Model G1101-*i* for monitoring at or near facilities utilizing GS for captured CO_2. To accomplish this goal, the experimental design included a combination of controlled gas challenges in an indoor laboratory environment and a sheltered ambient breeze tunnel, survey measurements for above-ground leak detection, and continuous ambient monitoring to provide performance data under a variety of simulated and real-world conditions.

Phase 1 of this verification test was conducted in Battelle laboratories in Columbus, OH to evaluate the analytical performance of the Model G1101-*i* under controlled laboratory conditions from July 9 through July 23, and August 11 through August 17, 2010. The Model G1101-*i* was challenged with gas standards of known isotopic composition and concentration to generate test samples over a range of CO_2 concentrations and isotopic compositions. The resulting concentration and δ^{13}C data were used to calculate accuracy, bias, linearity, precision, and response time, where appropriate. Bias with respect to ambient temperature and relative humidity (RH) was also assessed.

The ability of the Model G1101-*i* to detect CO_2 leaks was evaluated during Phase 2 of this verification test, which was conducted at Battelle's Ambient Breeze Tunnel (ABT) facility in West Jefferson, OH. The ABT was used to simulate leaks of ^{13}C-depleted CO_2 in ambient air under simulated field conditions. The Model G1101-*i* was installed inside the ABT and ambient

air was drawn through the tunnel at approximately 1.8 meters per second (m/s) and a stream of pure $^{12}CO_2$ at a fixed flow rate was periodically introduced into the ABT. By varying the $^{12}CO_2$ flow rate, the minimum detectable CO_2 leak rate was determined for several $\delta^{13}C$ values. In addition, ambient air reference samples were collected to determine the comparability of the Model G1101-*i* to CO_2 concentration and $\delta^{13}C$ reference methods. Testing for Phase 2 was conducted from July 28 through July 30, 2010.

The utility of the Model G1101-*i* for monitoring at GS sites was evaluated during Phase 3, which was conducted at a coal-fired power plant in West Virginia. The analyzer was installed in a shed near the sequestration wells and sampled ambient air drawn from near the main well head over a one-week period from August 2 through August 6, 2010. During that period, ambient air reference samples were collected to determine the comparability of the Model G1101-*i* to CO_2 concentration and $\delta^{13}C$ reference methods. The Model G1101-*i* was also installed in a hybrid sedan vehicle and operated using battery power to conduct mobile surveys of GS site transmission lines and infrastructure. Finally, the leak rate response was determined from an intentional release to simulate an above ground leak.

3.2 Test Site Descriptions

3.2.1 Ambient Breeze Tunnel

Details of the ABT are provided in the TQAP. Briefly, the ABT was designed to conduct controlled releases in ambient air with down-wind measurements and has dimensions of approximately 45m × 6m × 6m. A large blower was used to constantly draw ambient air through the ABT facility at 3400 m³/min, equivalent to wind speeds of approximately 1.8 m/s. Controlled leaks were generated near the inlet to the ABT and the Model G1101-*i* was installed near the exit of the ABT, downstream of the mixing baffle. The enclosed nature of the ABT provided for controlled unidirectional flows with no confounding cross-winds. Photographs of the Model G1101-*i* as installed in the ABT are shown in Figure 3. Panel A shows the Model G1101-*i* installed on a scaffolding platform, with the inlet positioned 1.4 m above the concrete floor. The opening for ambient air is visible in Panel A. The blowers are located at the end of the tunnel that is visible in Panel B (behind the analyzer). Pure $^{12}CO_2$ was released through the Teflon tube, shown in Panel B, which was positioned approximately 1.5 m above the floor. The mixing baffles are visible in both panels. The blower was turned on each morning and shut off in the evening.
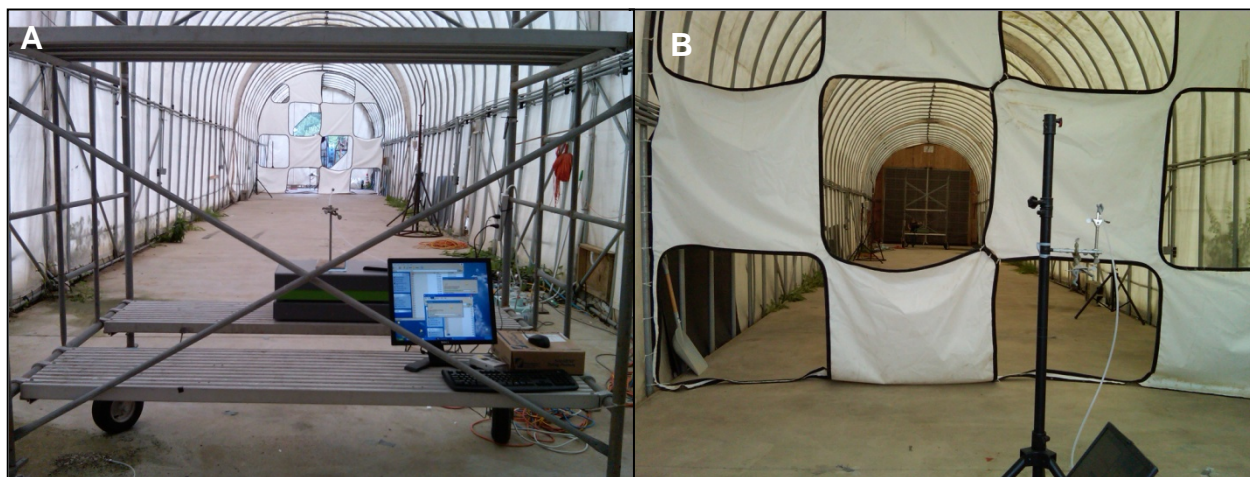
Figure 3. Photographs of the Model G1101-*i* installed in the ABT

3.2.2 GS Test Site

Details of the GS test site are provided in the TQAP. The GS test site was a West Virginia coal-fired power plant, where CO_2 from the flue gas is being captured, separated, compressed, and stored in a geologic formation over 7,000 feet below the surface. Due to an unplanned outage, the plant was not actively capturing or sequestering CO_2 during this verification test; however, captured CO_2 was present at elevated pressures in the transmission lines at the site. CO_2 in these lines was used for testing.

The Model G1101-*i* was installed in a shed near the above-ground CO_2 transmission lines, as shown in Figure 4 (Panels A and B), approximately 70 feet from the main injection well. Air was drawn into the shed to the Model G1101-*i* inlet through a length of Teflon tubing; the tubing inlet was positioned near the main injection well, as shown by the yellow circle in Figure 4, Panel C. The shed had a small window for ventilation and a wood floor in the front section where the analyzer was installed. Ambient temperatures during Phase 3 reached 37 °C and it became necessary to install an air conditioner inside the shed to reduce the indoor temperature. A MetOne meteorological station was installed approximately 15 feet from the transmission lines (Figure 4, Panel A).

Figure 4. Photographs of the GS test site

3.3 Experimental Design

Per direction from the vendor, the Model G1101-*i* was installed at each testing location by ETV testing staff using the instrument manual and without any specific training from the vendor (executed as designed). No on-site calibrations were performed. The vendor representative provided a list of parameters to be checked by verification testing staff on a daily basis to verify the operation of the Model G1101-*i* and identify signs of malfunction. The checklist, provided as Appendix A, was completed daily (Monday through Friday) by Battelle staff. In general, Battelle staff checked the status window for status messages, recorded several instrument parameter values, checked the analyzer flow rate, and backed up analyzer data.

For this verification test, all Model G1101-*i* readings were logged. The analyzer generated daily data files, which contained the raw readings as well as 30-second, 2-minute, and 5-minute running averages for $^{12}CO_2$, $^{13}CO_2$, and "delta" ($\delta^{13}C$). The measurement unit for CO_2 mole ratio (referred to in this report as concentration for convenience) is parts per million (ppm). The measurement unit for $\delta^{13}C$ is per mil (‰), or part per thousand.

The Model G1101-*i* also reported water vapor concentration and a number of instrument parameters. Each daily data file was 32.4 MB. In addition, select data were saved in smaller (~7 MB) files. Spectral data also generated by the analyzer were downloaded daily in case they would be needed for troubleshooting purposes. Spectral data files were generated hourly, with approximately 209 MB of zipped files per day. Data were downloaded daily to an external expansion drive, which was connected directly to the Model G1101-*i* by USB port. Approximately 13 GB of data were generated during this verification test, including spectral and regular data files.

During Phase 1, gas standard dilutions for each test condition were supplied to the Model G1101-*i* for a minimum of 20 minutes, unless otherwise noted. This allowed sufficient time for the flow from the dilution system to stabilize and the analyzer to record data record data under stable conditions to use for calculations. For the isotope bias tests, standards were delivered for a shorter period of time to conserve materials. For gas standard challenges, the average Model G1101-*i* value at each test condition was calculated from the last five minutes of raw data. The last five minutes were selected because the Model G1101-*i* response appeared to be stable during that period (i.e., a general increase or decrease in the response was not apparent). The average Model G1101-*i* response values were used in the calculations described in Chapter 5 of this report.

The Model G1101-*i* CO_2 concentration and $\delta^{13}C$ readings when sampling ambient air were compared to concurrent measurements using nondispersive infrared (NDIR) analysis and IRMS, respectively. Ten duplicate whole air samples were collected in glass flasks during Phases 2 and 3 of this verification test. Ambient air samples were collected by flushing the glass flasks for a period of five minutes and then pressurizing the flasks for one minute. For the comparisons, the Model G1101-*i* raw readings were averaged over the five minutes prior to the end of the pressurization period. For example, for a sample that was flushed from 4:49 to 4:54 PM and pressurized from 4:54 to 4:55 PM, the Model G1101-*i* raw readings were averaged from 4:50 to 4:55 PM and that average used for comparisons.

The Model G1101-*i* was verified by evaluating the parameters listed in Table 1. During all phases of this verification test, the Model G1101-*i* was operated by verification testing staff, who had read and who followed the instrument manual. No additional training was deemed necessary by the vendor. The ambient temperature and relative humidity in which the Model G1101-*i* was operated during all phases of this verification test were recorded using a Hobo data logger with temperature/RH probe. The performance of the Model G1101-*i* during this verification test are presented in Chapter 6 of this report and summarized in Chapter 7.

Table 1. Summary of Performance Parameters and Testing Frequency

Phase	Performance Parameter	Objective	Comparison Based On	Testing Frequency
1	Accuracy and Bias	Determine degree of quantitative agreement with compressed gas standard	Challenges with CO_2 gas standards of known $\delta^{13}C$ at 3 RH levels and 3 temperatures	-3 runs at each of 12 nominal concentrations (one $\delta^{13}C$ value) -1 run at each of 15 combinations of RH, temperature, and CO_2 concentration (one $\delta^{13}C$ value) -2 runs at each of 9 combinations of CO_2 concentration and $\delta^{13}C$)
1	Linearity	Determine linearity of response over a range of CO_2 concentrations	Dynamic spiking with gas standards	-3 runs at each of 12 nominal concentrations (one $\delta^{13}C$ value) -2 runs at each of 9 combinations of CO_2 concentration and $\delta^{13}C$)
1	Precision	Determine repeatability of successive measurements at fixed CO_2 levels	Repetitive measurements under constant facility conditions measured	-3 runs at each of 12 nominal concentrations (one $\delta^{13}C$ value)
1	Response Time	Determine 95% rise and fall time	Recording successive readings at start and end of sampling CO_2 gas standard	Once during each day of dynamic spiking testing
2	Minimum Detectable Leak Rate	Determine the minimum detectable CO_2 leak rate under controlled and ambient conditions	Repetitive measurements of a low-level $^{12}CO_2$ leak	Once
3	Leak Response Rate	Determine the amount of time between an intentional release of captured CO_2 and detection of the leak by the CO_2 analyzers	Recording the elapsed time between start of release and positive detection	Once
2	Comparability to Reference Method	Determine degree of quantitative agreement with reference method results	Concentration and $\delta^{13}C$ results for ambient air reference samples	2 sample pairs collected during ambient air sampling
3				8 sample pairs collected during ambient air sampling

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3.3.1 Accuracy, Bias, Precision, and Linearity

During Phase 1, the Model G1101-*i* was challenged with a series of dilutions from a compressed CO_2 gas standard (in CO_2-free zero air—ambient air filtered to contain less than 0.1 ppm of total hydrocarbons) to achieve measurements in the range of expected ambient air concentrations (i.e., 350 ppm) and also at higher concentrations (up to 5000 ppm CO_2) to simulate concentrations that could be observed in high hazard areas. Three non-consecutive measurements were recorded at each of twelve different nominal concentration levels at one $\delta^{13}C$ value. Each concentration was supplied to the analyzers for at least twenty minutes. Table 2 shows the CO_2 concentration values that were supplied to the analyzer, and the order in which the concentrations were supplied. As Table 2 indicates, the CO_2 concentrations were first supplied to the analyzers in increasing order, then in random order, and finally in decreasing order. Dilutions were prepared from a certified compressed mixture of 11% CO_2 in air (Air Liquide Acublend Master Class, 11.0% ±1%) using an Environics Model 6100 Multi-Gas Calibrator. These tests were conducted at room temperature without added humidity.

Table 2. CO_2 Concentrations and Order for Multi-point Challenges

Nominal CO_2 Concentration (ppm)	Measurement Number		
0	1	16	36
100	2	22	35
200	3	18	34
300	4	14	33
400	5	23	32
500	6	20	31
750	7	15	30
1600	8	17	29
2450	9	21	28
3300	10	19	27
4150	11	24	26
5000	12	13	25

The Model G1101-*i* response to the series of CO_2 gas standards was used to evaluate accuracy, bias, precision, linearity, and response time. The statistical procedures used are presented in Chapter 5. Accuracy was calculated at each concentration and for each replicate relative to the nominal CO_2 concentration. Bias was calculated once for the series of multi-point CO_2 challenges. The Model G1101-*i* precision was demonstrated by the reproducibility of the average Model G1101-*i* response at each nominal CO_2 concentration. Linearity was assessed by establishing a multi-point calibration curve from the Model G1101-*i* response and was determined once for the full range (0 to 5000 ppm) and once for the range of concentrations expected in ambient air (0 to 500 ppm).

3.3.2 Isotope Ratio Bias

Analyzer bias with respect to the $\delta^{13}C$ value was assessed by challenging the analyzers with dilutions from three CO_2 isotope mixtures [SMU Stable Isotope Laboratory, through Oztech Trading Corporation, -3.61 ‰; -10.41 ‰; and -40.80 ‰ (0.01 standard deviation)], each at three CO_2 concentrations (see Table 3). Dilutions were prepared using an Environics Model 6100 Multi-Gas Calibrator, which was calibrated for air. Since the CO_2 isotope mixtures were pure CO_2 and the dilution system's mass flow controllers are calibrated for air/nitrogen, a correction factor of 0.737 was applied to the input concentrations to account for differences in specific heat and density of CO_2 versus nitrogen. The resulting actual nominal CO_2 concentrations delivered to the Model G1101-i are shown in Table 3. Accuracy was calculated at each concentration and $\delta^{13}C$ value for each replicate relative to the nominal CO_2 concentration. Bias was calculated for each $\delta^{13}C$ value. Each CO_2 concentration/$\delta^{13}C$ pair was delivered to the analyzers twice for a total of 18 data points. Due to limitations imposed by the quantity of CO_2 isotope mixtures available from the vendor, two replicates were conducted instead of the three replicates prescribed in the TQAP for this verification test. This deviation from the TQAP resulted in a slightly smaller data set than originally planned, with only two replicates for each test condition instead of three. The average relative percent difference (RPD) for the two replicates was 0.8% for CO_2 concentration, with a range from 0.03% to 5.2%. For $\delta^{13}C$, the average RPD was 1.8%, with individual values ranging from 0.03% to 10.1%. Having more replicates could make it possible to see smaller differences in the Model G1101-i response due isotope bias, if any, over the analyzer's inherent reproducibility. In an effort to conserve the gas standard and maximize the data return, each dilution was delivered to the CO_2 analyzer for 10 minutes or the time required for the signal to stabilize plus 5 minutes, whichever was longer.

Table 3. CO_2 Concentrations and Isotope Ratios for Bias Tests

Approximate $\delta^{13}C$ (‰)	Input Nominal CO_2 Concentrations (ppm)	Actual Nominal CO_2 Concentrations (ppm)
-3.61 ± 0.01[a]	350	259
	500	370
	1000	740
-10.41 ± 0.01	350	259
	500	370
	1000	740
-40.8 ± 0.01	350	259
	500	370
	1000	740

(a)   Uncertainties are standard deviations reported on certificates of analysis for each gas standard.

3.3.3 Response Time

The data collected for the multi-point CO_2 challenges (Section 3.3.1) during Phase 1 were also used to determine the analyzer response time. The 95% rise time and 95% fall times were

calculated for the consecutive concentration steps (Table 2, measurements 1-12 and 25-36). Calculations for response time are described in Chapter 5.

3.3.4 *Temperature and RH Bias*

Bias due to the ambient and sample temperature and RH was assessed during Phase 1. The Model G1101-*i* was tested in a Webber temperature and RH-controlled chamber, which was used to vary the temperature and RH of the air surrounding the Model G1101-*i*. Dilutions of a CO_2 gas standard were delivered to the Model G1101-*i* (inside the chamber) at three concentrations got each of six temperature/RH condition. Dilutions were prepared from a certified compressed mixture of 11% CO_2 in air (Air Liquide Acublend Master Class, 11.0% ±1%) using an Environics Model 6100 Multi-Gas Calibrator. Humidified zero air was added to the output of the Environics calibrator to achieve the desired sample RH. The resulting mixture passed through a coil placed within the environmental chamber to assist with temperature equilibration upstream of the G1101-*i* inlet. The temperature and relative humidity of the sample stream was monitored using the Hobo data logger with temperature/RH probe, positioned downstream of the G1101-*i* inlet. The specific conditions are listed in Table 4. The Model G1101-*i* was subjected to each test condition once for a minimum of twenty minutes. One $\delta^{13}C$ value was used for these tests. Bias was calculated as described in Chapter 5.

Table 4. Chamber and Sample Conditions for Temperature and RH Bias Tests

Nominal		Sample		Chamber		Nominal CO_2
Temperature (°C)	RH (%)	Temperature (°C)	RH (%)	Temperature (°C)	RH (%)	Concentration (ppm)
20 ± 2°C	0 ±10%	20.1	0	19.8	10	350
		19.7	0	19.9	11[a]	500
		19.7	0	20.1	17[a]	1000
	50 ±10%	20.5	50	20.1	49	350
		20.5	54	20.1	49	500
		20.5	54	20.1	48	1000
	90 ±10%	21.3	91	20.5	84	350
		20.4	86	20.4	88	500
		20.4	88	20.1	86	1000
32 ± 2°C	50 ±10%	32.8	55	32.2	47	350
		32.8	52	32.0	48	500
		32.8	50	32.2	49	1000
	90 ±10%	32.8	91	32.2	87	350
		32.8	93	32.1	86	500
		32.8	90	32.1	87	1000
4 ± 2°C	50 ±10%	4.2	49	4.2	51	350
		4.2	50	4.1	50	500
		4.2	52	4.0	47	1000

(a)   Chamber conditions that were outside the target range specified in the TQAP.

During two temperature/RH bias runs at 20°C, the chamber RH conditions were outside the target range specified in the TQAP for this verification test (11 and 17% RH versus 0% ±10%). However, the gas supplied to the analyzer was within the target range for these runs (0% RH actual). The difference in RH for the "ambient" conditions within the chamber, which was a deviation from the TQAP, is not expected to impact the analyzer's response given that it was within the vendor-reported operating range.

3.3.5 Minimum Detectable Leak Rate

The ability of a monitoring technology to detect a CO_2 leak under real-world conditions will depend on the isotopic signature of the leaking CO_2, isotopic signature of the ambient air, meteorological conditions, sampling proximity, local CO_2 sources, and the monitoring technology performance. The minimum leak rate that can be detected above ambient variability and the precision of the Model G1101-*i* was determined under semi-controlled conditions during Phase 2. The Model G1101-*i* was installed in the Reference Sampling and Test Section of the ABT, which is shown in Figure 3, Panel A. During this test, most of the parameters described above were controlled or accounted for in the experimental design so the performance of the Model G1101-*i* could be evaluated under a well-defined set of conditions. A leak was considered to be successfully identified if an increase or decrease in the measured $\delta^{13}C$, greater than 2 times the variability in ambient $\delta^{13}C$, was measured by the Model G1101-*i* for the last 15 minutes of each leak simulation period. (The 15-minute period was selected to reduce the potential for impacts due to short-term disturbances, such as nearby vehicle traffic.) The ambient air $\delta^{13}C$ variability was determined from one hour of ambient air data measured by the Model G1101-*i* on the day of testing. Pure (99.95%) $^{12}CO_2$ was added to the ambient air diluent being drawn into the ABT to simulate a low-level leak of ^{13}C-depleted CO_2. This approach assumed that a low-level leak would be well-mixed in the ambient air diluent before reaching the Model G1101-*i*, which is expected for the flow conditions utilized during the testing (approximately 1.8 m/s velocity).

The initial $^{12}CO_2$ leak rate was set at a nominally detectable level that was twice the standard deviation (*s*) in $\delta^{13}C$ measured by the analyzer for a period of at least one hour on the day of testing. A leak at that rate was introduced for approximately 20 minutes with at least 15 minutes of ambient air flow between simulated leaks. An iterative process was used to slowly approach the minimum detectable leak rate, starting with a leak flow rate of 0.156 LPM $^{12}CO_2$, and increasing the flow rate until three leak simulation replicates were successfully identified. This leak rate was defined as the minimum detectable limit for the G1101-*i* under the test conditions. A conventional CO_2 analyzer used to monitor the CO_2 concentration in the ambient air diluent to assist in identifying changes in air mass or nearby CO_2 sources that could impact the CO_2 concentration or $\delta^{13}C$. Keeling plots were also investigated as a tool to evaluate the Model G1101-*i*'s ability to detect CO_2 leaks. Keeling regression analysis can be used to determine the $\delta^{13}C$ value for CO_2 source that periodically impacts the measurement location and was conducted by plotting the measured isotopic delta ($\delta^{13}C$) versus the inverse of the CO_2 concentration and conducting a linear regression analysis. The $\delta^{13}C$ value for CO_2 source(s) was given by the intercept of the regression line. Regression lines were calculated for data collected during the background ambient air measurements and during the leak simulations; the resulting intercept and 95% confidence interval of the intercept were compared to determine whether the $^{12}CO_2$ source could be detected.

The equivalent leak rate as a function of source $\delta^{13}C$ was also back-calculated for several relevant $\delta^{13}C$ values: −3.5‰, −20‰, and −35‰. This calculation assumed that the magnitude of the measured changes in $\delta^{13}C$ values from ambient levels were the same for the pure (99.95%) $^{12}CO_2$ and for the calculated leak levels for ^{13}C-depleted CO_2. This assumption allows the calculation of CO_2 release rate necessary to achieve the overall $\delta^{13}C$ change for a given $\delta^{13}C$ source value, knowing the ambient $\delta^{13}C$ value and the flow rate of air through the ABT. It should be noted that the use of a pure ^{12}C source for leakage (i.e., −1000 ‰) maximizes instrument sensitivity to $\delta^{13}C$, although not to total CO_2 concentration; thus, conditions during an actual leak would be different with respect to both $\delta^{13}C$ and total CO_2 concentration.

3.3.6 Ambient Air Monitoring

In the evenings and when the Model G1101-*i* was not undergoing testing during Phase 3, it was installed in the shelter near the GS wellhead and monitored ambient air. The purpose of this activity was to evaluate data completeness and operational factors during deployment for ambient monitoring. The ambient air measurements (CO_2 concentration and $\delta^{13}C$) and meteorological conditions are reported in Chapter 6 with summary statistics (average and standard deviation). The meteorological conditions could not be monitored continuously as stated in TQAP because the meteorological station stopped working overnight on August 4, 2010 for approximately 12 hours. The meteorological data provided supporting information, for example to plot CO_2 concentration data as a function of wind direction, but was not used specifically for evaluation of the performance parameters identified in the TQAP for this verification test. As a result, the missing data did not impact the evaluation of the analyzer's performance, although fewer data points were included in Figure 15 as a result of the malfunction.

While the Model G1101-*i* was installed near the wellhead, captured CO_2 that was present in the transmission lines, was intentionally released for a brief period. The leak rate response time, the time between initiation of the release and when the leak is detected by the Model G1101-*i* response, as described in Chapter 5, was determined.

3.3.7 Mobile Surveys

During Phase 3, the Model G1101-*i* was transported to road-accessible features of the GS, such as transmission lines and monitoring wells. The purpose of these tests was to evaluate the ease of use and operational factors of the analyzers during use in a mobile survey mode. The Model G1101-*i* was installed in the back seat of a Nissan Altima hybrid sedan and operated using power from a marine deep cycle/RV battery and power inverter. A Teflon inlet was extended out the rear window and held in place approximately one foot from the ground and one foot from the vehicle. The hybrid vehicle was operated in electric mode to the extent possible to avoid contamination of the inlet line with CO_2 from the vehicle exhaust and reduce ambiguity in the CO_2 sources being monitored. The vehicle was then driven to the features of interest listed in Table 5, below, with an effort to approach each feature from the downwind side while the vehicle was operating in electric mode. A Polar RS800CX with GPS capability was used to track vehicle speed and location during the mobile surveys.

Table 5. Mobile Survey Features

Feature Type	Number of Each Type
Above-ground transmission lines	1
Deep monitoring well	2
Injection well	2
Shallow aquifer monitoring well	7
Soil gas monitoring well	4

3.3.8 Comparability to Reference Method

The comparability of the Model G1101-*i* response was evaluated by comparing the analyzer response to the results of reference analyses for CO_2 concentration and $\delta^{13}C$, which were carried out by NOAA and by SIL-INSTAAR, respectively. CO_2 concentration measurements were conducted using NDIR analysis. The NDIR analysis method is described by Conway et al.[10] and Komhyr et al.,[11] and references therein. Calibration procedures and gases for the NDIR CO_2 analysis are described by Komhyr and coworkers.[11,12] The methods used for the carbon isotope ratio analysis are described in Trolier et al. [5] and Vaughn et al.[13] A detailed investigation of the calibrations, corrections, and overall uncertainties of the $\delta^{13}C$ analysis is presented in Masarie et al.,[14] in the context of an international intercomparison study of atmospheric measurements. The sampling and analytical procedures used for these reference measurements have been developed and documented over decades of research by NOAA and SIL-INSTAAR. Complete details of the reference method procedures and associated QA efforts are detailed in the references cited above and other references therein. A summary of the reference sample collection procedure is provided in the TQAP for this verification test (Deviation 3).

Two pairs of duplicate grab samples of ambient air were collected for reference analyses during Phase 2, and eight pairs of duplicate samples were collected during Phase 3. Samples were sent first to NOAA for the CO_2 concentration analysis and then to SIL-INSTAAR for carbon stable isotope analysis. The results of the reference method measurements on those 10 duplicate sample pairs were compared to the average CO_2 analyzer response recorded at the same time the samples were collected to assess the comparability of CO_2 analyzer, as described in Chapter 5.

3.3.9 Data Completeness

No additional test procedures were carried out specifically to address data completeness. This parameter was assessed based on the overall data return achieved by the Model G1101-*i* and was evaluated separately for mobile survey testing.

3.3.10 Operational Factors

Operational factors such as maintenance needs, calibration frequency, data output, sustainability factors such as consumables used, ease of use, repair requirements, and sample throughput were evaluated based on operator observations. Battelle testing staff documented observations in a laboratory record book (LRB) and data sheets. Examples of information to be recorded include

the daily status of diagnostic indicators for the technology; use or replacement of any consumables; the effort or cost associated with any maintenance or repair; vendor effort (e.g., time on site) for any repair or maintenance; the duration and causes of any technology down time or data acquisition failure; operator observations about technology startup, ease of use, clarity of the vendor's instruction manual, user-friendliness of any needed software, overall convenience of the technologies and accessories/consumables, and the number of samples that could be processed per hour or per day. These observations were summarized to aid in describing the technology performance in this report.

Chapter 4
Quality Assurance/Quality Control

QA/quality control (QC) procedures were performed in accordance with the QMP for the AMS Center and the TQAP for this verification test. As noted throughout Chapter 3, there were four deviations from the TQAP. These deviations and their impact are discussed in the previous sections. QA/QC procedures and results are described in the following subchapters.

4.1 Reference Method Quality Control

The National Oceanic and Atmospheric Administration (NOAA) Earth System Research Laboratory (ESRL) provided reference method CO_2 concentration and isotope ratio analyses in coordination with the Stable Isotope Laboratory (SIL) at the University of Colorado's Institute for Arctic and Alpine Research (INSTAAR) for this verification test during Phases 2 and 3. NOAA ESRL Global Monitoring Division is the World Meteorological Organization (WMO), Global Atmospheric Watch Central Calibration Laboratory (CCL) for CO_2. The quality of the reference measurements was assured by adherence to the requirements of the data quality indicators (DQIs) and criteria for the reference method critical measurements, including requirements to perform tank gas calibrations. Gas tank calibrations included participating in periodic round-robin analyses of external standard gas cylinders, monthly analysis of tanks spiked at known levels, and daily analysis of an internal standard consisting of dry atmospheric air obtained from a clean air site on Niwot Ridge in the Rocky Mountains, Colorado. Table 6 shows the results of test flask analyses conducted on the days when ambient samples for this verification test were analyzed for CO_2 concentration. Figure 5 shows test flask results for 2010, with the difference between the actual and expected concentration plotted on the y-axis. Figure 6 shows CO_2 results for tests of the portable sampling unit (PSU84M) used to collect the ambient air samples. A different nominal CO_2 concentration was supplied on each of the three dates shown. The red symbols indicate flasks filled directly from a cylinder of known mixing ratio (controls). The blue symbols indicate flasks filled from the same cylinder, but through the portable sampling unit. The heavy black line represents the known CO_2 value and the dashed lines indicate ± 0.1 ppm.

Estimates of uncertainty associated with the reference analyses for isotopic measurements of CO_2 are based on the standard deviation of the last 30 measurements, run over ten days, for the cylinder that is run as a known unknown. This method of determining the uncertainty provides an estimate of the short-term precision of the isotope ratio measurement. Figure 7 shows the IRMS precision check results for 161 runs; the reference analyses for this verification test were included in runs 3152 and 3156. Unflagged data are shown in blue, flagged data are white, and

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results for runs for this verification test are shown in red. Error bars are one standard deviation for triplicate measurements. The solid line shows the mean for 142 unflagged runs and the dashed lines are one standard deviation from the mean. Based on the results of these precision checks, the estimated uncertainty for runs 3152 and 3156 is 0.017‰ and 0.015‰, respectively.

Table 6. Test Flask Results on Days when References Samples were Analyzed

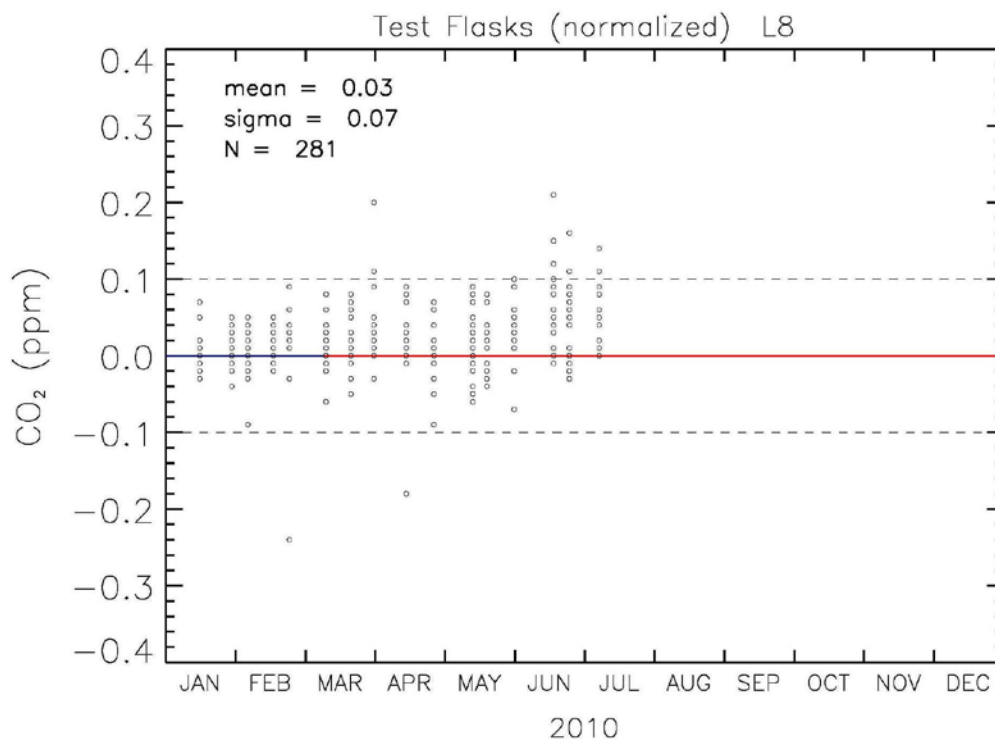| Flask Number	CO_2 Concentration (ppm)	Percent Recovery
Expected value	380.65	Not applicable
T26-99	380.65	100.00%
T4345-99	380.63	99.99%
T4453-99	380.67	100.01%
T4461-99	380.68	100.01%
T53-99	380.64	100.00%
T91-99	380.72	100.02%
Average	380.67	100.00%
Average Percent Difference	0.004%	

Figure 5. CO_2 Test Flask Results for 2010
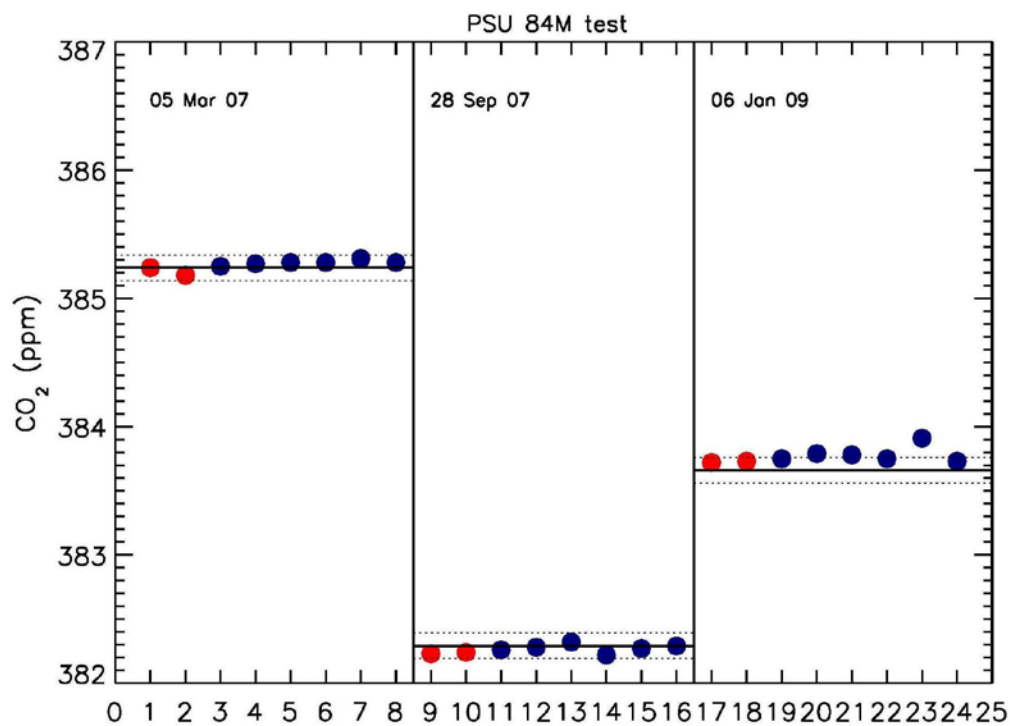
Figure 6. CO₂ Test Results for Portable Sampling Unit 84M
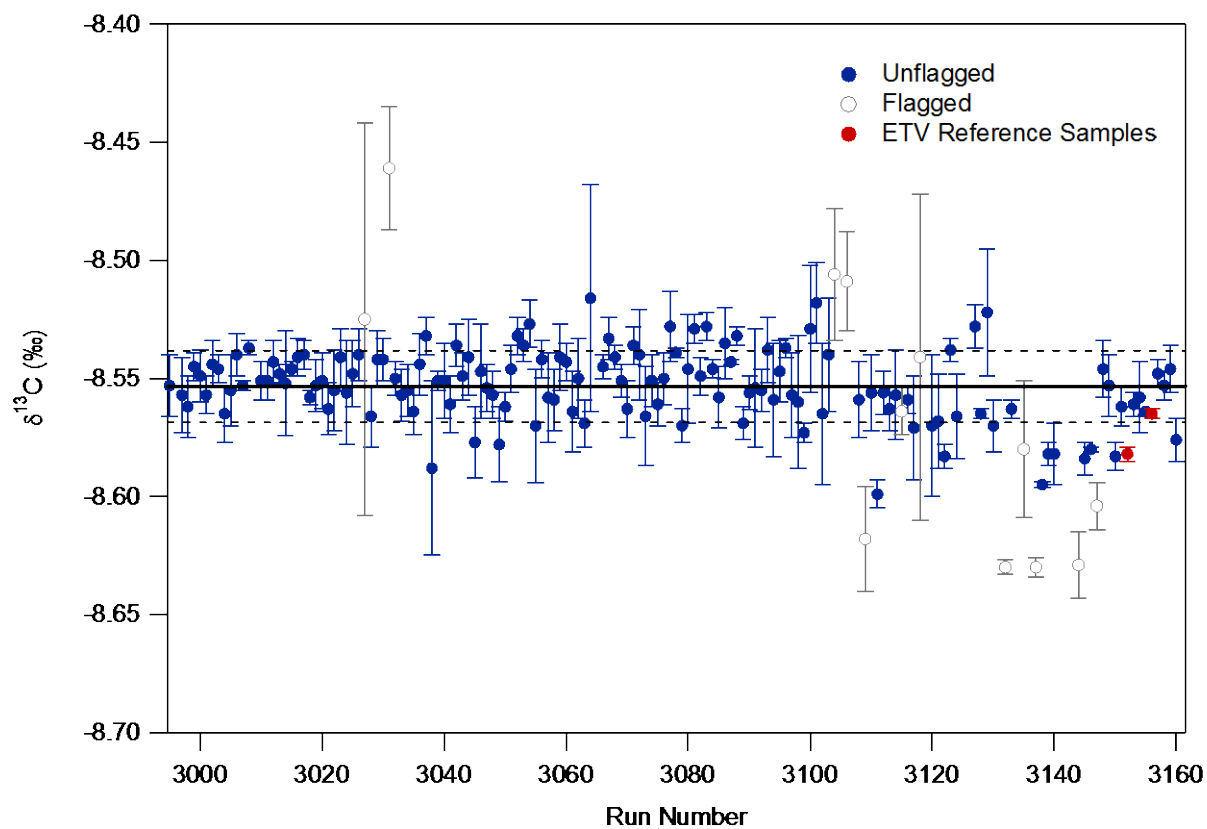
Figure 7. Isotope Ratio Precision Check Results

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NOAA and SIL-INSTAAR followed all standard QC procedures established for their respective ongoing programs of CO_2 and carbon isotope measurements, respectively. The results from those procedures, described above, are consistent with published results describing the long-term performance of these laboratories:

- The CO_2 concentration reference method should have an analytical precision better than 0.1 ppm: Analytical precision of approximately 0.05 ppm is reported from extensive data sets by Masarie et al.[14]

- The difference in CO_2 concentration for duplicate samples should be less than 0.5 ppm: Masarie et al. [14] report that the average difference in results for CO_2 between duplicate ambient air flask samples is 0.05 ± 0.12 ppm. The average difference between duplicate ambient air flask samples for this verification test was 0.38 ppm with a range of 0.02 to 1.95 ppm.

- Accuracy for CO_2 concentration measurements should be better than 1%: A 7-year intercomparison study of NOAA CO_2 measurements with those conducted by the Commonwealth Scientific and Industrial Research Organization (CSIRO) of Australia showed agreement within 0.21 ± 0.26 ppm.[14] This result is equivalent to agreement within approximately 0.06%. Analyses of synthetic mixtures will be less accurate due to pressure broadening and other effects.[12, 15, 16, 17]

- Stable carbon isotope measurements should have analytical precision better than ±0.02‰: The dual inlet IRMS method is reported to have a precision of ± 0.01‰, based on several hundred QC analysis runs conducted during routine analysis of ambient sample sets.[13]

- Stable carbon isotope analyses on duplicate samples should differ by less than 0.05‰: The replicate precision for carbon isotope ratios in duplicate samples is comparable to that in replicate analyses (i.e., ± 0.01‰). The average difference between duplicate ambient air flask samples for this verification test was 0.03‰ with a range of 0 to 0.072‰.

Although some of the duplicate sample results varied more than expected for CO_2 concentration and carbon isotope ratio (up to 0.072‰ as compared to the expected <0.05‰), the results are considered to have sufficient accuracy and precision to be used as a standard against which to evaluate the Model G1101-*i* responses in ambient air.

4.2 Phase 2 Leak Flow Rate Quality Control

A data quality indicator (DQI) was established for leak flow rate accuracy in Phase 2 to ensure that data used to support the quantitative performance evaluations of the CO_2 analyzers were of sufficient quality. During Phase 2, the accuracy of the leak flow rate was verified during each simulated leak test using an independent flow transfer standard. The acceptance criteria for the measured value to be within $\pm 10\%$ of the independent flow transfer standard. Actual results were for the leak flow rate determined to be the minimum detectable by the Model G1101-*i* was

0.423 LPM. The flow rate was measured by an independent calibrated flow meter (DryCal DC-2) was 0.4526 LPM. The relative percent difference (RPD) between the two values was 1.7%.

4.3 Dynamic Dilution System Quality Control

Many of the testing activities utilized gas standards of known CO_2 concentration and/or isotopic composition to prepare multiple mixtures that were then delivered to the Model G1101-*i*. The Model G1101-*i* was then evaluated against the calculated composition of the resulting mixture. For example, a 500 ppm CO_2 mixture was prepared by diluting 9.1 standard cubic centimeters per minute (sccm) of an 11% ±1% CO_2 standard to 2000 sccm using an Environics 6100 dilution system. The concentration accuracy of the dilution system is reported at ±1.0% of the setpoint when the mass flow controllers are operating between 10% and 100% of full scale flow.[18] The calibration of the Environics 6100 dilution system was checked prior to the verification test against a DH Instruments Moblox Flow Terminal. The calibration was conducted by the Battelle Instrument Services Laboratory, which is accredited to the International Organization for Standardization (ISO) 17025 standard. The uncertainty of the flow standard used for the calibration was 0.2% of the reading. All flows tested (4 per flow controller) were within 1% of the set point; therefore, the calibration was not adjusted. Given these values, one would expect that the uncertainty of the concentrations delivered from the Environics 6100 would be ±3% of the reading, which accounts for uncertainty in flows from two flow controllers used to prepare each dilution and in the gas standard accuracy. As discussed in Section 4.4.1, the reference method analyses of dilutions prepared by this system had an uncertainty (95% confidence level, or two times the standard deviation) that is 3-4 times larger than this estimate. The overall uncertainty in the prepared concentrations is therefore estimated to be ±7% (95% confidence level).

The accuracy of the isotope ratio as a result of dilution is known only for samples that were analyzed by the SIL as dilution may unintentionally fractionate isotopes. Dilutions from one isotope mixture were analyzed by the reference method and found to be within 1.12% of the expected value (see Section 4.4.1). These dilutions were prepared at total flow rates (16.5 LPM) higher than used to evaluate the Model G1101-*i* (approximately 5 LPM) and only at concentrations near ambient levels (see Table 7); it is not known whether fractionation affected dilutions used to evaluate the Model G1101-*i*.

4.4 Audits

Three types of audits were performed during the verification test: a performance evaluation (PE) audit of the CO_2 concentration and isotope ratio reference methods, a technical systems audit (TSA) of the verification test procedures, and a data quality audit. Audit procedures are described further below.

4.4.1 Performance Evaluation Audit

The PE audit of the CO_2 reference methods (concentration and isotope ratio) was performed by supplying to each reference method four independent CO_2 standards (in duplicate) provided by Battelle. The four PE samples are summarized in Table 7, below. PE samples were prepared by

diluting certified gas standards [−10.41‰ pure CO_2 compressed gas standard (SMU Stable Isotope Laboratory, through Oztech Trading Corporation) and 11.0% ±1% CO_2 in air (Air Liquide Acublend Master Class)] with Alphagaz Zero Air using a calibrated dilution system. The diluent was supplied to the reference method sampling inlet, with excess flow vented to atmospheric pressure, and collected in glass flasks in the same manner as ambient air samples. The PE samples were analyzed for CO_2 in the same manner as for all other ambient air samples and the analytical results for the PE samples were compared to the nominal concentration/isotope ratio. The actual results are presented in Table 7. The root mean square of the differences between the nominal value and the reference method is 3.4% and all were within the target criterion (30%) for this verification test. The audit samples were supplied to the reference laboratories with the ambient air samples from the verification test. Since the reference methods were carried out by laboratories that hold the WMO CCL for CO_2, reference method results are considered to be the true value.

Table 7. PE Sample Results for CO_2 Concentration and Isotope Ratio

	Concentration (ppm)			Carbon Isotope Ratio (‰)		
Sample	**Nominal**	**Reference Method Result**	**Percent Difference**	**Nominal**	**Reference Method Result**	**Percent Difference**
1	329.9	334.61	1.4%	−10.41	−10.293	−1.12%
		334.11	1.3%		−10.295	−1.10%
2	379.8	378.74	−0.3%	−10.41	−10.304	−1.02%
		378.91	−0.2%		−10.340	−0.67%
3	349.8	329.51	−5.8%	Not certified;	−37.009	NA
		329.34	−5.8%	evaluated for	−37.014	
4	392.8	379.93	−3.3%	concentration	−36.980	NA
		379.80	−3.3%	only	−37.032	

4.4.2 Technical Systems Audit

The Battelle AMS Center Quality Assurance Officer for this verification test performed a TSA during the both the laboratory and field testing portions of this verification test to ensure that the verification test was performed in accordance with the QMP for the AMS Center and the TQAP. The EPA Quality Manager also observed field testing.

The TSA of the laboratory portion of the verification test was performed on July 9, 12, 15, and 22, 2010 at Battelle's Air Quality and Temperature/Humidity Chamber Laboratories in Columbus, OH. During this TSA, the Battelle AMS Center Quality Assurance Officer observed verification testing staff conducting tests for concentration accuracy, isotope bias, and temperature/RH bias.

The TSA of the field testing portion of the verification test was performed on August 5, 2010 at the GS site. During this TSA, the Battelle AMS Center Quality Assurance Officer observed verification testing staff complete the analyzer daily checklist, troubleshoot the meteorological station, collect ambient air samples, and load the Model G1101-*i* analyzer into the Nissan Altima hybrid sedan in preparation for mobile survey tests.

The TSA of both the laboratory and field testing portions resulted in 3 findings and 5 observations. The first finding was that quantity of gas standards available on July 15, 2010 for the isotope ratio bias tests at −3.61 per mil CO_2 may have been insufficient to conduct triplicate runs. To address this finding, which also applied to other tests, additional materials were purchased, the time at each test condition was shortened, and the third replicate at each isotope ratio/concentration combination was removed from the test. This finding was also addressed in Deviation 1 as described in Section 3.3.2. The second finding was that the RH values in the environmental chamber exceeded the limits described in the TQAP for two test conditions. This finding was addressed in Deviation 2 and is described in Section 3.3.4 of this report. The third finding was that the meteorological conditions could not be monitored continuously as stated in TQAP because the meteorological station stopped working overnight on August 4, 2010 for approximately 12 hours. The cause of the problem was investigated and the meteorological station started working on August 5, 2010. This finding was addressed in Deviation 4 and described in Section 3.3.6 of this report. The observations were related to vendor training, instability in the dilution system flow rates, inconsistencies in the Model G1101-*i* response to zero air, apparent slow analyzer response to varying test conditions, and calibration of the independent flow meter. In response to these observations, the following actions were taken:

- Documentation of the vendor's instructions regarding training of verification testing staff was provided to the Battelle AMS Center Quality Assurance Officer and included in the project files
- Performance of the Environics 6100 was investigated and a faulty pressure regulator discovered and replaced
- Troubleshooting revealed that CO_2 present in the dilution system's internal components diffused into the zero air stream; an alternate method for delivering zero air by bypassing the dilution system was identified and utilized; affected testing was repeated
- Care was taken to ensure that internal components of the Environics dilution system were thoroughly flushed prior to starting tests after switching the CO_2 source (compressed gas cylinder)
- The flow meter in use was sent out to be calibrated and a different flow meter was used for the remainder of the verification test.

TSA reports were prepared and copies were distributed to the EPA.

4.4.3 Data Quality Audit

Records generated in the verification test were reviewed before these records were used to calculate, evaluate, or report verification results. Data were reviewed by a Battelle technical staff member involved in the verification test. The person performing the review added his/her initials and the date to a hard copy of the record being reviewed.

100% of the verification test data was reviewed for quality by the Verification Test Coordinator, and at least 10% of the data acquired during the verification test and 100% of the calibration and QC data were audited. The data were traced from the initial acquisition, through reduction and statistical analysis, to final reporting to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked.

A data audit report was prepared and a copy was distributed to the EPA.

Chapter 5
Statistical Methods

The statistical methods used to evaluate the quantitative performance factors listed in Section 3.3 are presented in this chapter. The average Model G1101-*i* response values (Y) used in the calculations presented in this section were calculated from the last 5 minutes of each testing condition (e.g., CO_2 gas standard challenge) from the analyzer's raw data (~0.5 Hz) unless otherwise indicated. Qualitative observations were also used to evaluate verification test data.

5.1 Model G1101-*i* Factor Calibration Correction

The dependence of the delta value measured by Model G1101-*i* on CO_2 concentration is defined by a constant that is determined during factory calibration tests. For the Model G1101-*i* that was evaluated in this verification test, an incorrect value (−0.01686) was input into the software. This error was reported to the Verification Test Coordinator by Picarro. The error was allowed to be corrected because the notification of correction was distributed to all users of Picarro instruments that had been calibrated during that factory calibration test and was not something that was identified based on the verification test data. To address this error, the values for $\delta^{13}C$ were corrected using Equation 2, which was provided by Picarro:

$$\delta_{corrected} = \delta_{reported} + A + \frac{B}{^{12}CO_2} \tag{2}$$

where A is equal to -4.86‰ and B is 2156 ppm.

5.2 Water Vapor Correction

Water vapor can interfere with the measurement of the carbon dioxide concentration and isotope ratios in the following ways:

- Dilution – The dilution effect is simply the change in mixing ratio of CO_2 caused by variability in the humidity. For example, a dry air mass traveling over warm water will accumulate humidity, and this additional water vapor will dilute the concentration of the other gases. Conversely, a humid air mass that becomes drier (as through precipitation) will cause an inverse dilution effect, increasing the mixing ratios of the other gases. Because it affects ^{12}C and ^{13}C equally, dilution affects only the concentration, not the reported isotope ratio. The magnitude of the effect is a 1% decrease in the reported fractional concentration

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for every 1% increase in water vapor concentration. The dilution effect is largely due to the most abundant isotopolog of water ($^1H_2^{16}O$), which is 99.8% of all the water under most conditions.

- Spectral broadening – The Lorentzian broadening of the spectral lines are affected by the presence or absence of water vapor. The magnitude of the effect on the reported concentrations is of the order of the dilution effect (though generally somewhat smaller). The effect on each of the two lines (i.e., the ^{12}C and ^{13}C spectral lines) is not necessarily identical, leading to a systematic error in the reported isotope ratio as a function of water vapor concentration. The effect on delta is proportional to water vapor concentration and independent of CO_2 concentration. As with dilution, this effect is largely due to $^1H_2^{16}O$.
- Direct spectral interference – Direct spectral interferences are caused by any water vapor spectral lines that are in the immediate vicinity of either the ^{12}C or ^{13}C spectral lines. These can cause offsets to these two gas species that affect both the concentration and reported isotope ratio. The effect on delta is proportional to the product of the water vapor concentration and inversely proportional to the carbon dioxide concentration. Unlike dilution, this effect can depend on whichever isotopolog or isotopologs are interfering with the ^{12}C and ^{13}C measurements.

Consequently, corrections for water vapor were made to the data reported by the G1101-*i* before the data were used in calculations described here or otherwise reported.

5.2.1 Delta Water Vapor Correction

Reported Model G1101-*i* values for delta were post-corrected for water vapor interferences using Equation 3:

$$\delta_{corrected\_wv} = \delta_{corrected} - H_2O_{reported} \times \left(-0.67 + \frac{850}{^{12}CO_{2_{wet}}}\right) \tag{3}$$

where $\delta_{corrected}$ is the corrected delta value (Equation 1), and $^{12}CO_{2wet}$ and $H_2O_{reported}$ are the corresponding $^{12}CO_2$ concentration and water vapor molar ratio (%v) reported by the Model G1101-*i* , respectively. The resulting delta value, $\delta_{corrected\_wv}$ was used for the calculations described in the following sections.

5.2.2 CO₂ Concentration Water Vapor Correction

Reported Model G1101-*i* values for CO_2 concentration ($^{12}CO_{2wet}$) were corrected for water vapor dilution using Equation 4:

$$\frac{^{12}CO_{2_{wet}}}{^{12}CO_{2_{dry}}} = 1 + \left(\mu' + \frac{m'}{^{12}CO_{2_{wet}}}\right) \times H_2O_{reported} \tag{4}$$

where μ' equal to −0.01527, m' is 0.358, and $H_2O_{reported}$ is the corresponding water vapor molar ratio reported by the Model G1101-*i*.

Equation 5 was used to calculate total (12 + 13) CO_{2dry}:

$$CO_{2dry} = {}^{12}CO_{2dry} + {}^{13}CO_{2dry} \qquad (5)$$

where, as derived from Equation 1:

$$^{13}CO_{2dry} = {}^{12}CO_{2dry} \times \left[{}^{13}C/{}^{12}C_{PDB} \times \left(\frac{\delta_{corrected\_wv}}{1000} + 1 \right) \right]$$

The resulting concentration value, CO_{2dry}, and the water vapor-corrected delta value ($\delta_{corrected\_wv}$) were used in the calculations described in the following sections and reported in Chapter 6.

5.3 Accuracy

Accuracy of the Model G1101-i concentration response with respect to the individual CO_2 gas standard dilutions was assessed as the percent recovery (%R), using Equation 6:

$$\%R = \left[1 + \left(\frac{Y-X}{X} \right) \right] \times 100 \qquad (6)$$

where Y is the average measured CO_2 analyzer value (CO_{2dry}) and X is the nominal CO_2 gas standard concentration. The average, minimum, and maximum %R values are reported for each series of multi-level CO_2 challenges. The accuracy of the analytical standards, as certified by the manufacturer, is also reported.

The calculation for %R implies that the error would scale with the magnitude of the measured value, which is true for concentration measurements. However, error in the isotope ratio does not scale with the magnitude of the delta value, which is arbitrarily set based on a recognized standard. Therefore, the accuracy of the Model G1101-i with respect to isotope ratio was determined as the difference between the Model G1101-i measured value and the certified standard (nominal $\delta^{13}C$) value.

5.4 Bias

Bias of the Model G1101-i is defined as a systematic error in measurement that results in measured error that is consistently positive or negative compared to the true value. The bias was calculated as the average percent difference (%D) of the Model G1101-i response compared to the nominal CO_2 gas standard value (with respect to concentration and isotope ratio) and was calculated for each series of multi-point CO_2 challenges and isotope ratio bias tests, using Equation 7:

$$\%D = \frac{1}{k} \sum_{j=1}^{k} \left(\frac{Y-X}{X} \right)_j \times 100 \qquad (7)$$

where k is the number of valid comparisons, and Y and X are the same as stated in 5.3. For temperature and RH bias, the comparison for concentration and isotope ratio utilized the values measured by the CO_2 analyzer at 20°C without added water vapor (dry conditions) as the "known" value.

The calculation for %D implies that the error would scale with the magnitude of the measured value, which is true for concentration measurements. However, error in the isotope ratio does not scale with the magnitude of the delta value, which is arbitrarily set based on a recognized standard. Therefore, the accuracy of the Model G1101-*i* with respect to isotope ratio was determined as the difference between the Model G1101-*i* measured value and the certified standard (nominal $\delta^{13}C$) value.

5.5 Precision

The precision of the Model G1101-*i* was evaluated from the triplicate responses to each CO_2 gas standard supplied during the multi-point challenges (summarized in Table 2 and Table 3). The precision is defined as the percent relative standard deviation (%RSD) of the triplicate measurements and calculated for each CO_2 concentration and isotope ratio listed in Table 2 and Table 3, respectively, using Equation 8:

$$\%RSD_i = \frac{s}{\overline{Y_i}} \times 100 \tag{8}$$

where $\overline{Y_i}$ is the average Model G1101-*i* response at CO_2 concentration or isotope ratio *i*, and s the standard deviation of the analyzer responses at that concentration. The overall average %RSD was also calculated for each series of multi-point CO_2 challenges (with respect to CO_2 concentration) and for each gas standard (with respect to CO_2 $\delta^{13}C$) included the %RSD for all CO_2 concentrations tested for each gas source.

The calculation for %RSD implies that the error would scale with the magnitude of the measured value, which is true for concentration measurements. However, error in the isotope ratio does not scale with the magnitude of the delta value, which is arbitrarily set based on a recognized standard. Therefore, the accuracy of the Model G1101-*i* with respect to isotope ratio was determined as the difference between the Model G1101-*i* measured value and the certified standard (nominal $\delta^{13}C$) value.

5.6 Linearity

Linearity with respect to concentration and isotopic ratio was assessed by a linear regression analysis of the gas challenge data using the calculated CO_2 concentrations or $\delta^{13}C$ as the independent variable and the CO_2 analyzer results as the dependent variable. The results of the gas challenge tests were plotted and linearity was expressed in terms of slope, intercept, and coefficient of determination (R^2).

5.7 Minimum Detectable Leak Rate

The minimum detectable leak rate that represents the minimum level successfully identified by each of three trials was determined experimentally and all trial results are reported in Chapter 6. The equivalent leak rate at several $\delta^{13}C$ values of interest were calculated based on the flow rate of CO_2 that would be needed to give the same change in measured $\delta^{13}C$ with respect to ambient air (approximately $-8‰$).

The relative difference in stable carbon isotope from the PDB standard, referred to as $\delta^{13}C$, is calculated as shown in Equation 1 and expressed in ‰, or part per thousand.

$$\delta^{13}C_{Sample} = \left(\frac{^{13}C/^{12}C_{Sample}}{^{13}C/^{12}C_{PDB}} - 1\right) \times 1000 \tag{1}$$

Using Equation 4 and inputs for ambient air concentration (391.62 ppm), ambient air $\delta^{13}C$ (-7.13), $^{13}C/^{12}C_{PDB}$ (0.011237), a leak source CO_2 concentration (100% or 1×10^6 ppm), a leak source $\delta^{13}C$ value ($-35‰$, $-20‰$, and $-3.5‰$,), a leak flow rate (e.g., 0.423 LPM), and a total flow rate, the $\delta^{13}C$ value for ambient air with a prescribed leak were calculated. Microsoft Excel was used to create a spreadsheet that calculated the interim variables needed to determine the final predicted $\delta^{13}C$ for ambient air with a specific CO_2 leak. In the spreadsheet, the total flow rate was adjusted from the ABT value (3.40×10^6 LPM) to the total flowrate needed to accurately predict the difference between ambient and ambient air with the 0.423 LPM $^{12}CO_2$ leak simulated during the verification test ($\delta^{13}C = 0.808‰$). The resulting flow rate, 1.28×10^6 LPM, was used for the subsequent calculations. Using the same spreadsheet, Microsoft Excel's Goal Seek function was used to set the difference in detected $\delta^{13}C$ to ± 0.808 by varying the leak flow rate. This was tested first for 99.95% $^{12}CO_2$ and repeated for three leak source $\delta^{13}C$ values ($-35‰$, $-20‰$, and $-3.5‰$).

In addition, the $\delta^{13}C$ values measured by the Model G1101-i analyzer was plotted versus the inverse of the CO_2 concentration (i.e., in Keeling plots) and the uncertainty (95% confidence interval) in the intercept determined. Separate regressions were calculated for the background measurement period and leak simulations. Theoretically, the intercept will represent the isotopic ratio of the leak source. The intercept and uncertainty for the background measurement period and leak simulations were compared for each day of testing to determine whether the $^{12}CO_2$ source could be detected (i.e., the intercept for the leak simulation regression fell outside the background measurement period's intercept confidence interval.

5.8 Response Time

Response time was assessed in terms of both the rise and fall times (with respect to CO_2 concentration) of the Model G1101-i when sampling CO_2 gas standards. The rise time (i.e., 0% to 95% response time) was determined by recording all CO_2 analyzer readings as the gas supplied to the analyzers is switched between CO_2 standards of increasing concentration. Once a stable response has been achieved with the gas standard, the fall time (i.e., the 100% to 5%

response time) was determined in a similar way, by recording all CO_2 analyzer readings as the CO_2 concentration in the gas supplied is reduced in concentration. Rise and fall times were determined once during multi-point gas challenges and reported in units of seconds and minutes.

The leak response time was calculated as the time elapsed between the start of the intentional CO_2 release and two different outcomes: 1) when a visible increase in CO_2 concentration was observed in the data and 2) when an alarm limit of 1,000 ppm had been reached. In addition, the leak response time with respect to isotope ratio was determined as the time between the start of the intentional release and when a value for $\delta^{13}C$ that was at least 2 standard deviations different from the average ambient value was reached.

5.9 Comparability

Comparability between the Model G1101-*i* results and the reference method results for both CO_2 concentration and carbon isotope ratio were calculated in terms of accuracy and bias using Equation 1 and Equation 2, respectively, for these performance parameters.

5.10 Data Completeness

Data completeness was assessed based on the overall data return achieved by the Model G1101-*i* during the testing period. The calculation will use the total number of hours during which apparently valid data was reported by the Model G1101-*i* divided by the total number of hours when data could potentially have been collected during the entire field period. The causes of any incompleteness of data return were established from operator observations or vendor records, and noted in the discussion of data completeness results in Chapter 6.

Chapter 6
Test Results

The results of the verification test of the Model G1101-*i* are presented in this section. The analyzer logged raw data (~0.5 Hz) as well as 30-second, 2-minute, and 5-minute running averages of the instantaneous CO_2 concentration and $\delta^{13}C$ readings. The Model G1101-*i* was operated using the factory calibration. Any differences between the factory calibration and the certified gas standards would be manifested in the accuracy, bias, and potential comparability performance parameters evaluated during this verification test; other performance parameters such as the linearity coefficient of determination, precision, and response time would not be impacted by differences in gas standards or calibration methods because of the nature of the calculations. All Model G1101-*i* measurement data were corrected for an error in the factory-set calibration (affecting the delta value only) and water vapor as described in Chapter 5. CO_2 concentrations are the sum of $^{12}CO_2$ and $^{13}CO_2$. Negative CO_2 concentration values should be considered the result of differences in gas standards used to calibrate the Model G1101-*i* and the gas standards used to evaluate the analyzer during this verification test. Negative CO_2 concentration values can also be caused by drift in the Model G1101-*i* response. Error bars shown on the x-axes represent flow rate accuracy of the Environics system that was used to prepare the gas standard dilutions. Errors due to isotope fractionation or other artifacts have not been quantified.

6.1 Concentration Accuracy and Bias

Accuracy checks were conducted during Phase 1 of the verification test. The Model G1101-*i* was challenged with dilutions from a compressed CO_2 standard at concentrations between 100 and 5,000 ppm. The standard was diluted with zero air and delivered to the Model G1101-*i* through a Teflon tube at a flow rate of 2 LPM; excess flow was vented to atmospheric pressure.

Figure 8 presents the CO_2 concentrations recorded by the Model G1101-*i* during the concentration accuracy check gas challenges, along with the nominal CO_2 concentration levels supplied to the analyzer. The averages of the last 5 minutes (approximately 250 data points) of measurements at each test condition and the calculated %R values are presented in Table 8. The SD for each measured concentration is also reported for reference purposes. As shown in Table 8, %R values ranged from 90.0 to 113%. Except at concentrations less than 300 ppm, the Model G1101-*i* response was lower than the nominal value. Bias in the Model G1101-*i* concentration response to CO_2 gas standards was assessed for the accuracy checks and was −3.98%. Given the uncertainty estimate for the nominal CO_2 concentrations of ±7%, it is not

possible to determine from these measurements alone whether the observed inaccuracies and biases are due to errors in the instrument response or the gas preparation.
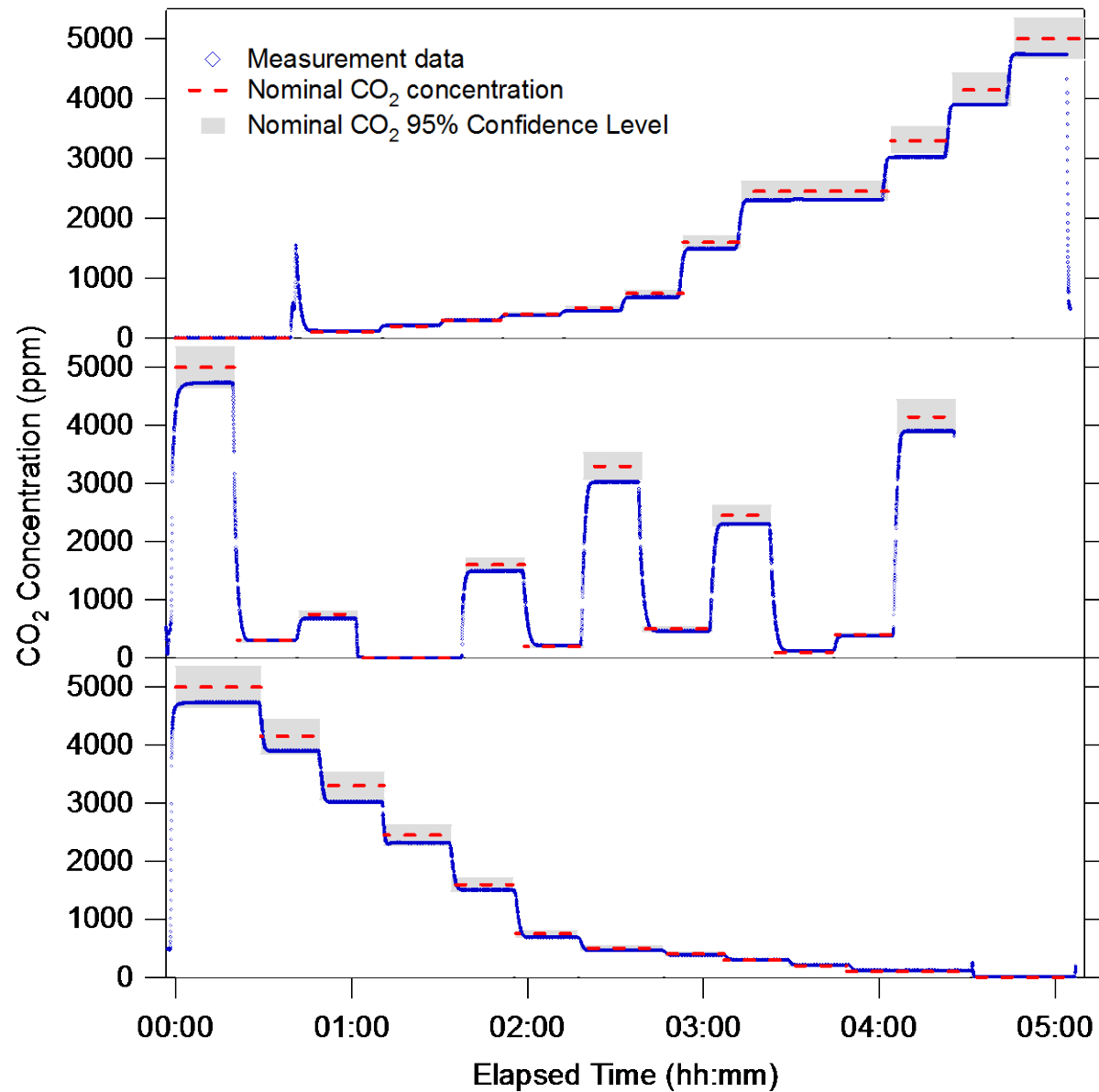
Figure 8. Model G1101-*i* Concentration Accuracy Results

Table 8. Concentration Accuracy Results

Measurement Number	CO$_2$ Gas Standard Concentration (ppm)	Average G1101-*i* (12+13)CO$_2$ Response (ppm)	SD (ppm)	%R
1	0	0.1[a]	0.1	NA[b]
2	100	110.6	0.2	110
3	200	205.8	0.2	102
4	300	295.9	0.2	98.6
5	400	374.5	0.2	93.6
6	500	452.8	0.2	90.6
7	750	675.0	0.2	90.0
8	1600	1491.8	0.3	93.2
9	2450	2304.0	0.4	94.0
10	3300	3019.2	0.4	91.5
11	4150	3901.2	0.6	94.0
12	5000	4735.2	0.5	94.7
13	5000	4725.1	0.6	94.5
14	300	297.9	0.2	99.3
15	750	675.7	0.2	90.1
16	0	0.9	0.1	NA
17	1600	1491.2	0.3	93.2
18	200	207.6	0.3	104
19	3300	3017.7	0.3	91.4
20	500	455.1	0.2	91.0
21	2450	2301.5	0.5	93.9
22	100	113.1	0.2	113
23	400	375.5	0.2	93.9
24	4150	3897.3	0.6	93.9
25	5000	4730.2	0.6	94.6
26	4150	3894.2	0.5	93.8
27	3300	3012.9	0.5	91.3
28	2450	2304.4	0.3	94.1
29	1600	1494.9	0.4	93.4
30	750	677.9	0.2	90.4
31	500	454.7	0.2	90.9
32	400	376.1	0.2	94.0
33	300	297.1	0.2	99.0
34	200	207.2	0.2	104
35	100	111.3	0.2	111
36	0	0.6	0.1	NA
Average				96.0
Minimum				90.0
Maximum				113
Bias (%D)				−3.98

(a) Data in this table are reported to the number of significant digits appropriate for the analyzer's reported accuracy and precision

(b) NA = Not applicable

6.2 Concentration Precision

Table 9 presents the calculated precision of the Model G1101-*i* determined from the average responses to the triplicate challenges at each CO_2 concentration level during the concentration accuracy checks. The precision of the Model G1101-*i* response varied from 0.1% to 1.2%. The highest %RSD value was observed for the lowest concentration standard (100 ppm). The average precision was 0.3%. The precision of the Environics 6100 gas dilution system is not specified by the vendor. It is therefore not possible to determine from these measurements alone whether the observed precision was limited by the G1101-*i* instrument or the gas dilution system.

Table 9. Concentration Precision Results

CO_2 Gas Standard Concentration (ppm)	Overall Average G1101-*i*(12+13)CO_2 Response (ppm)	%RSD
0	0.5[a]	NA[b]
100	111.7	1.2%
200	206.9	0.5%
300	297.0	0.3%
400	375.4	0.2%
500	454.2	0.3%
750	676.2	0.2%
1600	1493	0.1%
2450	2303	0.1%
3300	3017	0.1%
4150	3898	0.1%
5000	4730	0.1%
Average %RSD		0.3%

(a) Data in this table are reported to the number of significant digits appropriate for the analyzer's reported accuracy and precision
(b) NA = Not applicable

6.3 Concentration Linearity

Figures 9 and 10 show the linearity results for the concentration accuracy checks. A linear regression was calculated from the results presented in Table 8 (average Model G1101-*i* response versus nominal CO_2 gas standard concentration) over the range of 0 to 5,000 ppm and from 0 to 400 ppm. The 95% confidence interval for the slope and the intercept of each line was also calculated (shown in the following text within parenthesis). For 0 to 5,000 ppm, the slope of the regression line was 0.938 (±0.006), with an intercept of −1.32 (±13.6) and R^2 value of 0.9997. For the 0 to 400 ppm data set, the slope of the regression line was 0.935 (±0.036), with an intercept of 11.3 (±8.9) and R^2 value of 0.9958. As shown in Figures 9 and 10, the 95% CI for the regression line includes the 1:1 line for concentrations less than approximately 950 ppm.
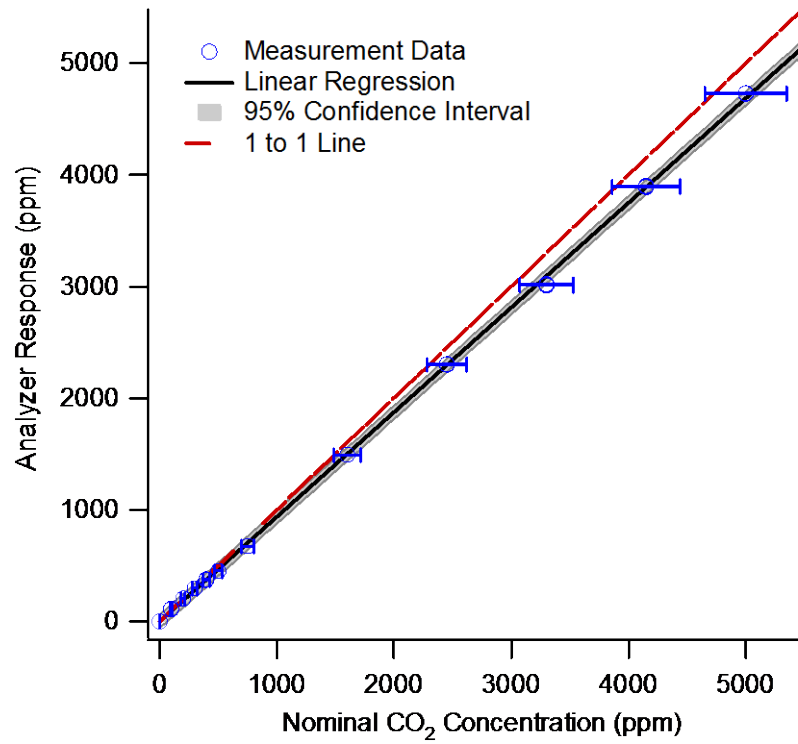
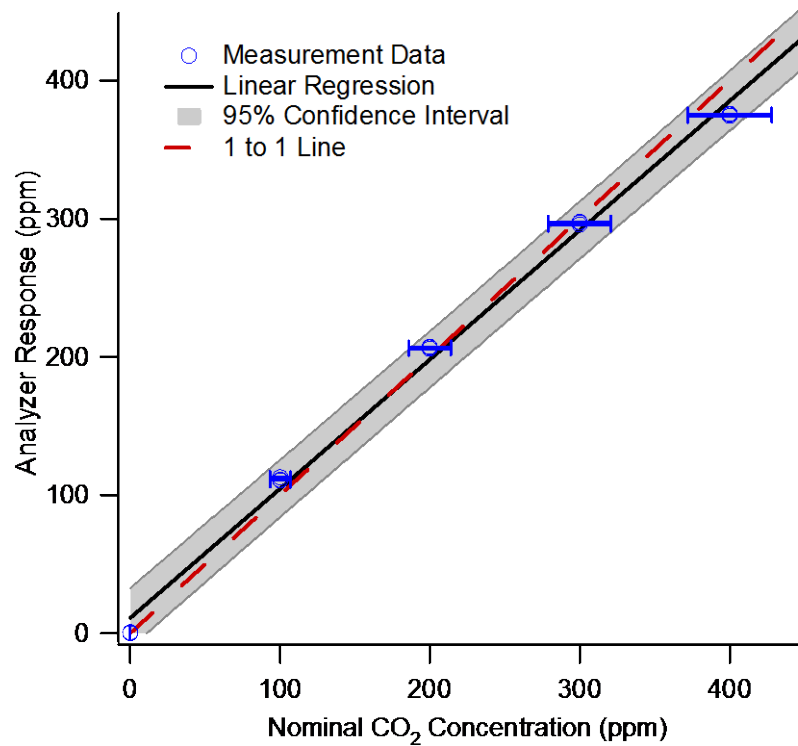**Figure 9. Model G1101-*i* Concentration Linearity Results**

Figure 10. Model G1101-*i* Concentration Linearity Results

6.4 Response Time

Response time was determined during the concentration accuracy checks from the amount of time required for the Model G1101-i to reach 95% of the change in response for the sequentially increasing and decreasing test conditions shown in Figure 7. The 95% rise and fall times are presented in Table 10. The average 95% rise time was 2.43 minutes and the 95% fall time was 2.53 minutes. Response times were calculated from raw (unaveraged) data. It is not possible to determine from these measurements alone whether the observed response time is limited by the response of the Model G1101-i or the gas dilution system.

Table 10. Response Time Results

Measurement Number	CO_2 Gas Standard Concentration (ppm)	95% Rise Time		95% Fall Time	
		(seconds)	(minutes)	(seconds)	(minutes)
1	0	NA[a]	NA		
2	100	(b)	(b)		
3	200	134.0[c]	2.23		
4	300	133.2	2.22		
5	400	159.8	2.66		
6	500	161.8	2.70		
7	750	160.7	2.68		
8	1600	163.8	2.73		
9	2450	174.4	2.91		
10	3300	96.6	1.61		
11	4150	123.4	2.06		
12	5000	112.2	1.87		
25	5000			130.6	2.18
26	4150			141.7	2.36
27	3300			90.0	1.50
28	2450			159.8	2.66
29	1600			179.9	3.00
30	750			174.0	2.90
31	500			158.4	2.64
32	400			178.6	2.98
33	300			168.9	2.82
34	200			217.5	3.63
35	100			67.3	1.12
36	0			130.6	2.18
Average		142.0	2.37	151.5	2.53
Minimum		96.6	1.61	67.3	1.12
Maximum		174.4	2.91	217.5	3.63

(a) NA = Not applicable
(b) Could not be calculated due to interruption in gas flow to connect analyzer to dilution system.
(c) Data in this table are reported to the appropriate number of significant digits based on precision of the analyzer's reported data.

6.5 Isotope Ratio Accuracy and Bias

Isotope ratio accuracy was evaluated during Phase 1. The Model G1101-*i* was challenged with dilutions from three certified CO_2 isotope mixtures: −3.60‰, −10.41‰, and −40.80‰. The standards were diluted with zero air using the Environics 6100 dilution system and delivered to the Model G1101-*i* through a Teflon tube at a flow rate of 5 LPM; excess flow was vented to atmospheric pressure. Higher total flow rates were used for this test to accommodate flow rate limits of the dilution system.

Table 11 presents the average $\delta^{13}C$ response recorded by the Model G1101-*i* during the isotope ratio accuracy check gas challenges, along with the nominal $\delta^{13}C$ and CO_2 concentration levels supplied to the analyzer. The averages of the last 5 minutes (approximately 250 data points) of measurements at each test condition and the calculated absolute differences from the expected value are presented. The SD for each measured concentration is also reported for reference purposes. As shown in Table 11, the differences ranged from 1.1 to 2.7‰. The lowest absolute differences were observed for the −40.80‰ standard and at the higher CO_2 concentrations. Figure 11 shows the isotope ratio absolute differences plotted as a function of CO_2 concentration for each $\delta^{13}C$ value. The strongest correlation between concentration and measured isotope ratio was observed for the −3.60‰ standard, with an R^2 value of 0.9468, a slope of −0.0025 and intercept of 3.24.

Table 11. Isotope Ratio Accuracy Results

Gas Standard Isotope Ratio (‰)	Gas Standard Concentration (ppm)	Isotope Ratio (‰)			
		Average G1101-*i* Response (‰)	SD	Difference from Standard (‰)	Average Difference (‰)
−3.60	259	−0.9[a]	2.2	2.7	2.1
	370	−1.2	1.6	2.4	
	740	−2.2	0.8	1.4	
	370	−1.6	1.8	2.0	
	740	−2.3	0.8	1.3	
	259	−1.0	2.2	2.6	
−10.41	259	−8.6	2.0	1.8	1.5
	370	−9.1	1.9	1.3	
	740	−9.2	0.9	1.2	
	370	−9.0	1.6	1.4	
	740	−9.3	0.9	1.1	
	259	−8.5	2.3	1.9	
−40.80	259	−39.0	2.0	1.8	1.4
	370	−39.7	1.6	1.2	
	740	−39.7	0.8	1.1	
	370	−39.1	1.5	1.7	
	740	−39.7	0.9	1.1	
	259	−39.0	2.0	1.8	
Average			1.5	1.7	
Minimum			0.8	1.1	
Maximum			2.3	2.7	

(a) Data in this table are reported to the number of significant digits appropriate for the analyzer's reported accuracy and precision.
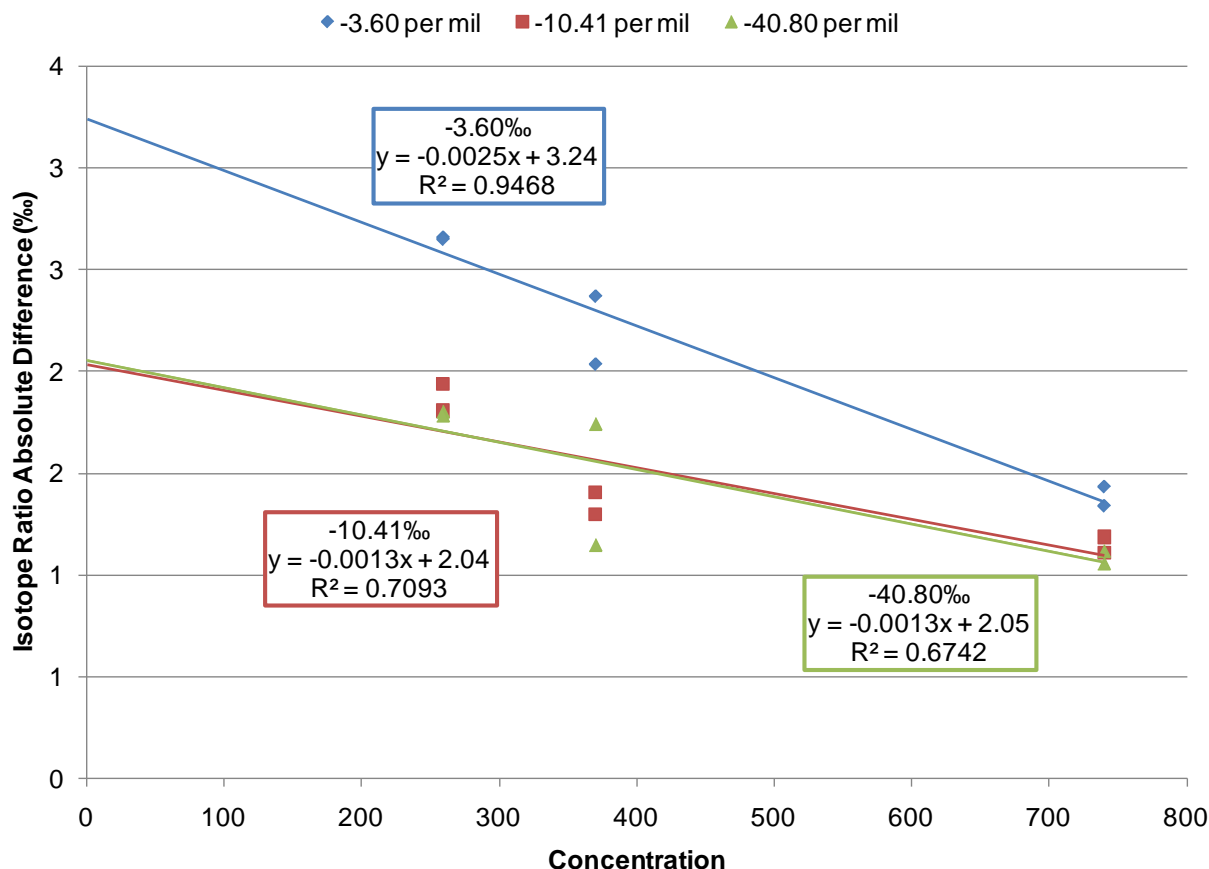
Figure 11. Model G1101-*i* Isotope Ratio Accuracy Results

6.6 Isotope Ratio Linearity

Figure 12 shows the linearity results for the isotope ratio accuracy checks. A linear regression was calculated from the results presented in Table 12 (average Model G1101-*i* response versus nominal CO_2 gas standard $\delta^{13}C$) for $-3.60‰$, $-10.41‰$, and $-40.80‰$ standards. The 95% confidence interval for the slope and the intercept of each line was also calculated (shown in the following text within parenthesis). The slope of the regression line was 1.01 ($\pm$ 0.02) with an intercept of 1.88 ($\pm$ 0.37) and R^2 of 0.9992. As shown in Figure 12, the 95% confidence interval of the regression line falls just above the 1 to 1 line.
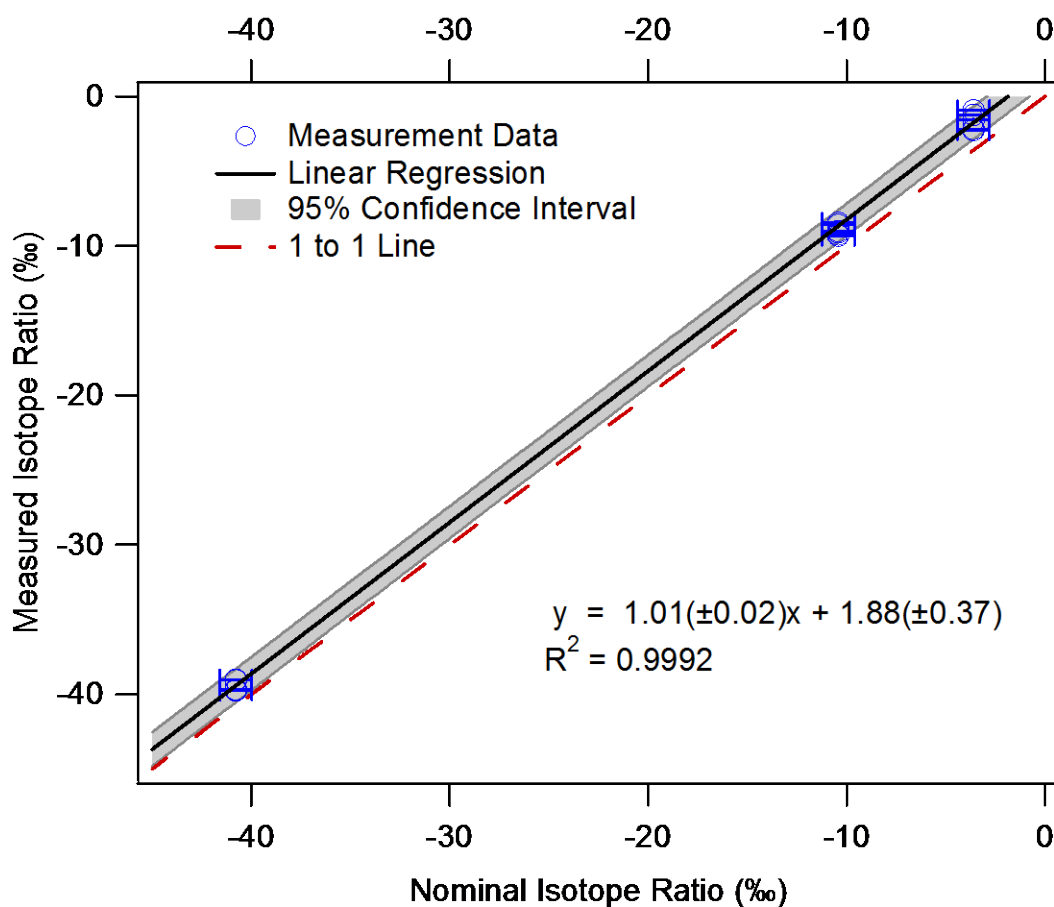
Figure 12. Model G1101-*i* Isotope Ratio Linearity Results

6.7 Temperature and RH Bias

Results for the temperature and RH bias tests are summarized in Table 12. To focus only on the impact of temperature and RH on the measurements, both concentration and $^{13}\delta C$ values at the various temperature and RH combinations were compared to the Model G1101-*i* results at 20°C and 0% RH. Bias was calculated for each temperature/RH combination and included in Table 12. In general, variability in ambient temperature and RH conditions resulted in bias values of 3% or less for Model G1101-*i* concentration measurements; isotope ratio values were within 0.7‰ of the value observed at 20°C and 0% RH. The maximum concentration bias value, 3.0%, was observed for CO_2 concentration at 4°C/50% RH. The largest isotope ratio average difference of 0.7‰ was observed for 32°C/90% RH. Given the uncertainty estimate for the nominal CO_2 concentrations of ±7%, it is not possible to determine from these measurements alone whether the observed non-linearity is due to errors in the instrument response or the gas preparation.

Table 12. Temperature and RH Bias Results

Nominal			Concentration			Isotope Ratio (‰)		
Temp-erature (°C)	RH (%)	Conc. (ppm)	Response (ppm)	%R	Bias (%D)	Response	Differ-ence	Avg Differ-ence
20 ± 2°C	0 ±10%	350	324.5	100.0		−35.0	0.6	
		500	447.6	100.0	0.0%	−35.8	−0.2	0
		1000	935.6	100.0		−36.1	−0.5	
	50 ±10%	350	327.8	101.0		−34.9	0.7	
		500	452.5	101.1	1.1%	−35.6	0.0	0.1
		1000	946.0	101.1		−36.0	−0.4	
	90 ±10%	350	333.4	102.7		−34.5	1.1	
		500	456.4	102.0	2.1%	−35.2	0.4	0.4
		1000	952.0	101.7		−36.0	−0.4	
32 ± 2°C	50 ±10%	350	333.9	102.9		−34.4	1.1	
		500	457.6	102.2	2.5%	−35.1	0.5	0.4
		1000	957.2	102.3		−36.0	−0.4	
	90 ±10%	350	334.1	102.9		−34.2	1.3	
		500	459.8	102.7	2.7%	−34.8	0.8	0.7
		1000	959.4	102.5		−35.6	−0.0	
4 ± 2°C	50 ±10%	350	337.6	104.0		−35.3	0.3	
		500	460.2	102.8	3.0%	−35.8	−0.2	−0.2
		1000	957.3	102.3		−36.3	−0.7	

(a) Data in this table are reported to the number of significant digits appropriate for the analyzer's reported accuracy and precision.

6.8 Minimum Detectable Leak Rate

Testing for the minimum detectable leak rate took place during Phase 2 at the ABT over the course of three days. The testing involved simulation of a pure $^{12}CO_2$ leak. The following factors that impact leak detestability were controlled or characterized: isotopic signature of the leaking CO_2 (99.95% $^{12}CO_2$), isotopic signature of the ambient air (measured), meteorological conditions (constant 1.8 m/s velocity in ABT), and sampling proximity to leak (fixed). The impact from CO_2 sources was limited by observing activity, primarily vehicular traffic, near the ABT. Control of those factors allowed for evaluation of the Model G1101-*i* performance for leak detection under a well-defined set of conditions. As described in Section 3.3.5, $^{12}CO_2$ was added to the ambient air diluent being drawn into the ABT to simulate a low-level leak of ^{13}C-depleted CO_2. The results of the testing are summarized in Table 13. The $^{12}CO_2$ flow rate was increased gradually from 0.156 LPM to 0.423 LPM, where it was detected successfully three times. Thus, the minimum detectable leak rate under the conditions of this verification test was 0.423 LPM. Time series plots for each day of testing are included in Figures 13, 14, and 15. In each figure, the upper panel shows CO_2 concentration measurements reported by the Model G1101-*i* (blue line) and by the LI-COR LI-820 NDIR CO_2 Analyzer (green line). The Model G1101-*i* $\delta^{13}C$ are shown (black trace) on the lower panel (primary axis). The gray shaded areas show periods when $^{12}CO_2$ was released and the leak flow rate (lower panel, secondary axis). The

red lines show the Model G1101-*i* average $\delta^{13}C$ response. Visual comparison of the Li-Cor CO_2 measurements, which were conducted upstream of the $^{12}CO_2$ leak, and the Model G1101-*i* data suggests that there was no detectable CO_2 concentration change with the addition of the relatively low flow rate of $^{12}CO_2$. This was an expected result based on calculations of the expected CO_2 concentration change.

Table 13. Minimum Detectable Leak Rate Results

Date	2SD Ambient Air $\delta^{13}C$ Variability (‰)	$^{12}CO_2$ Flow Rate (LPM)	Average Model G1101-i $\delta^{13}C$ Response (‰)	Ambient Air Average $\delta^{13}C$ (‰)	$\delta^{13}C_{leak}$ - $\delta^{13}C_{ambient}$ (‰)	Leak Detected?
		0	$-6.1^{(a)}$			
		0.156	-5.8	-5.7	-0.1	No
		0	-5.4			
		0.311	-5.9	-5.4	-0.5	No
		0	-5.5			
7/28/2010	0.549	0.349	-5.7	-5.4	-0.3	No
		0	-5.3			
		0.349	-5.8	-5.2	-0.6	Yes
		0	-5.2			
		0.349	-5.8	-5.1	-0.7	Yes
		0	-4.9			
		0	-7.9			
		0.423	-8.4	-7.4	-1.1	Yes
		0	-6.8			
		0.423	-7.4	-6.6	-0.8	Yes
7/29/2010	0.545	0	-6.5			
		0.423	-7.0	-6.2	-0.8	Yes
		0	-5.8			
		0.423	-6.2	-5.4	-0.8	Yes
		0	-5.0			
		0	-5.5			
		0.623	-6.0	-5.2	-0.8	Yes
		0	-4.9			
7/30/2010	0.632	0.623	-5.7	-4.8	-0.8	Yes
		0	-4.8			
		0.623	-6.0	-4.8	-1.2	Yes
		0	-4.8			

(a) Data in this table are reported to the number of significant digits appropriate for the analyzer's reported accuracy and precision.
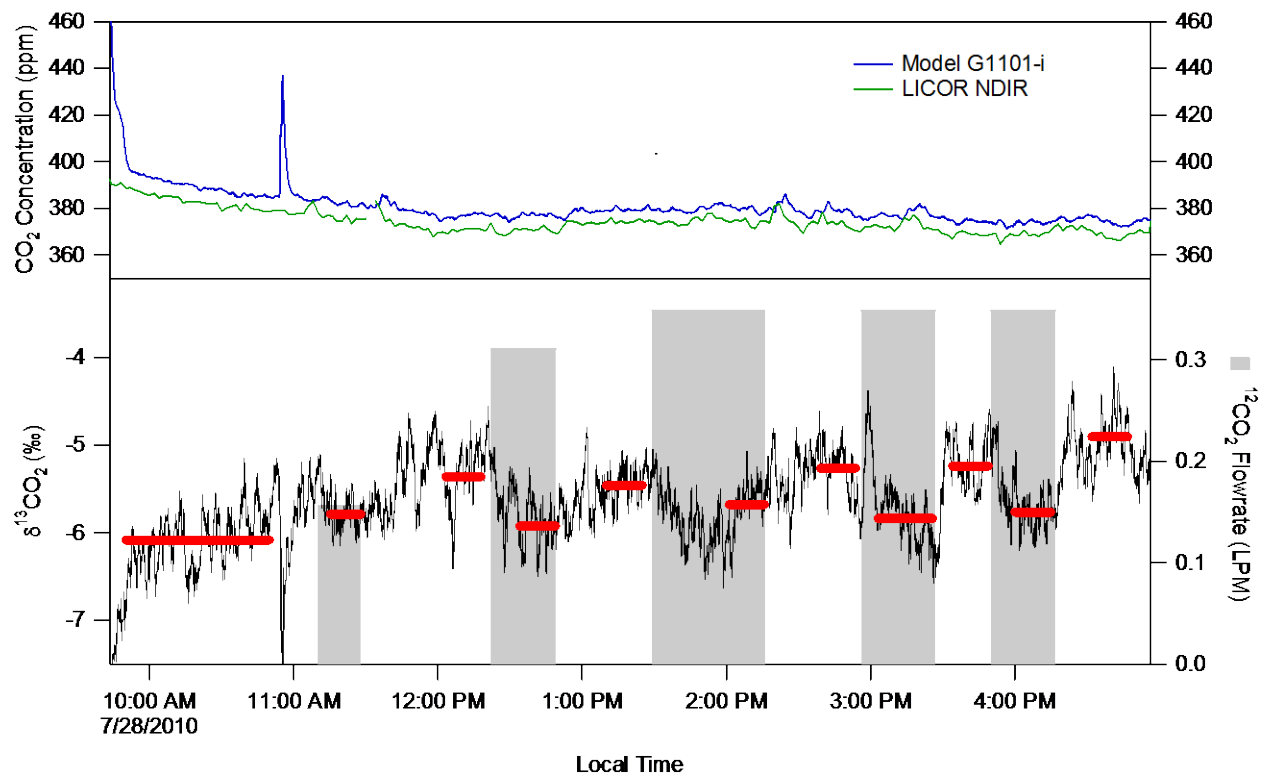
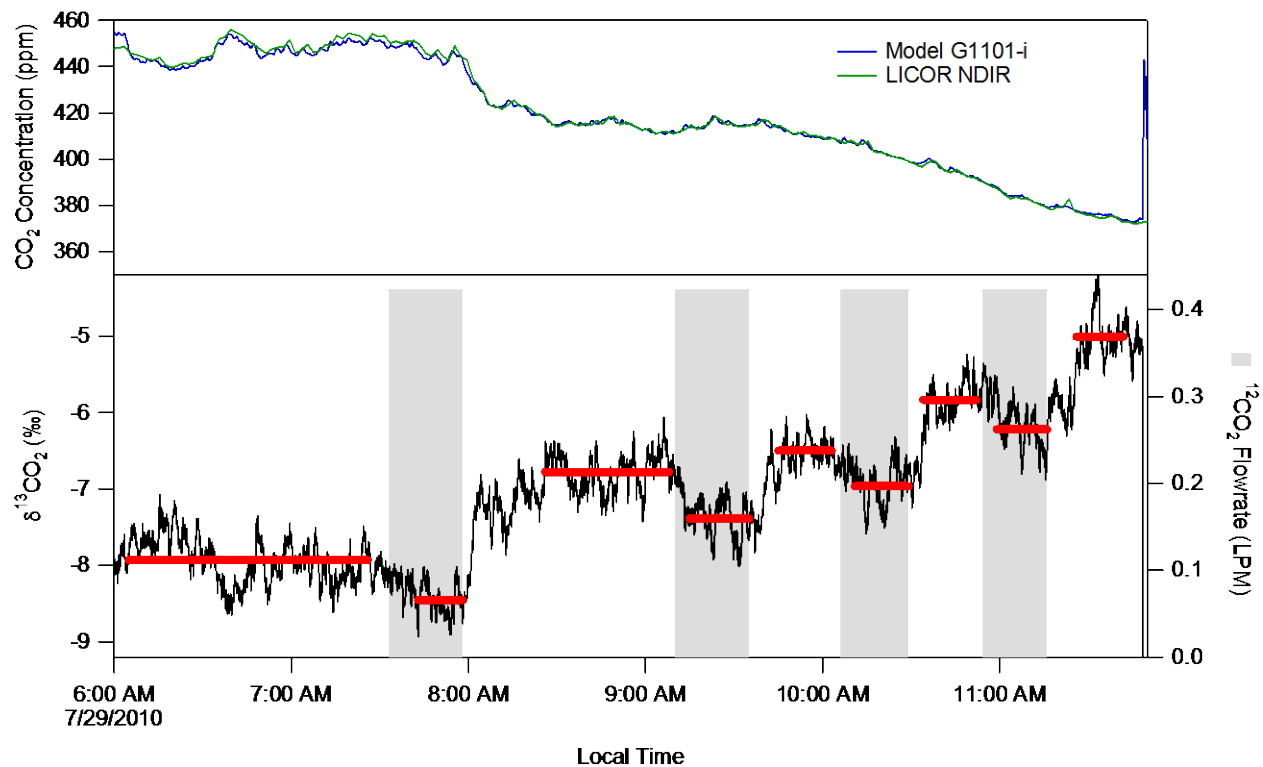**Figure 13. Model G1101-*i* Minimum Detectable Leak Rate Results for Day 1 (7/28/2010)**

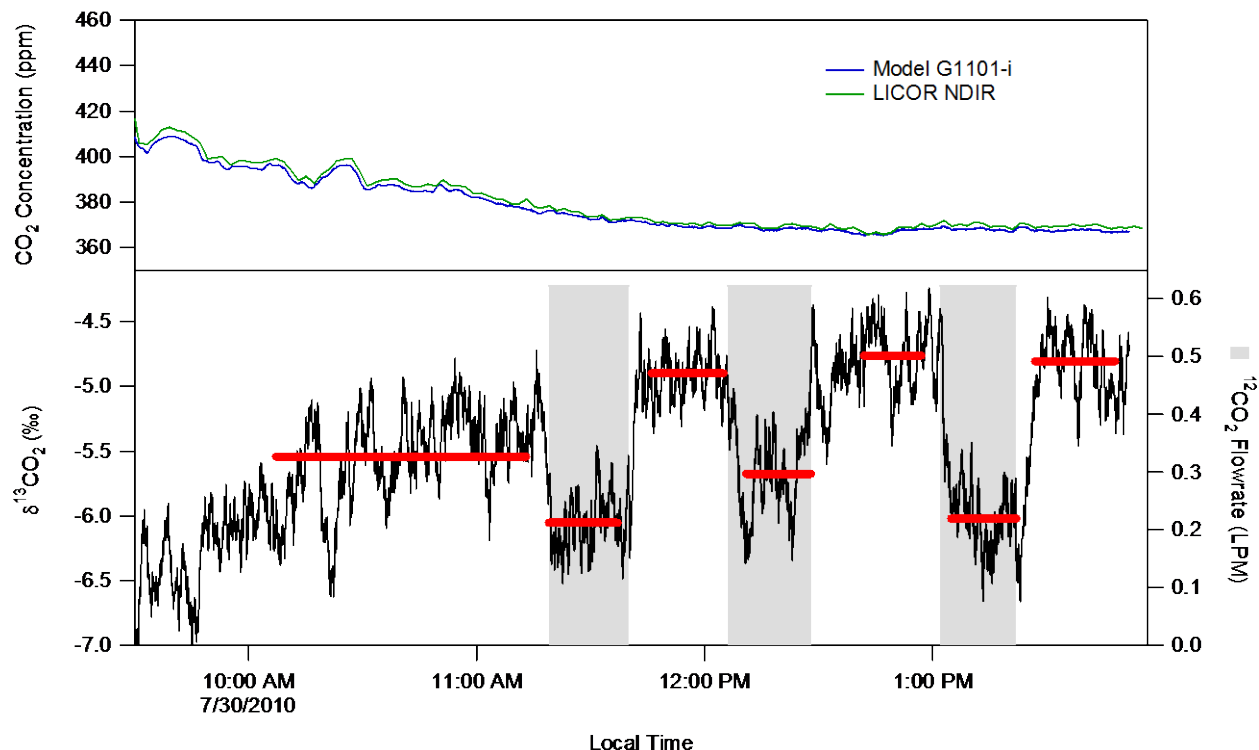**Figure 14. Model G1101-*i* Minimum Detectable Leak Rate Results for Day 2 (7/29/2010)**

Figure 15. Model G1101-*i* Minimum Detectable Leak Rate Results for Day 3 (7/30/2010)

For each day of testing, Keeling plots (δ^{13}C versus inverse CO_2) were generated for background monitoring and leak simulation test data. Linear regressions were calculated separately for each day's background and test data, as shown in Figures 16. Background data from all three days of testing are shown together; leak simulation data for each day are plotted separately. The intercept, which represents the isotopic signature of the CO_2 source, and 95% confidence interval for each day of testing are summarized in Table 14. While the intercepts for leak simulation test data did not fall within the confidence interval for the same day's background data, suggesting that a different CO_2 source was impacting the site during leak simulation testing, the absolute value of the intercepts were closer to that for the background data (−22.8‰) than for a pure ^{12}CO2 source (−955.5‰).
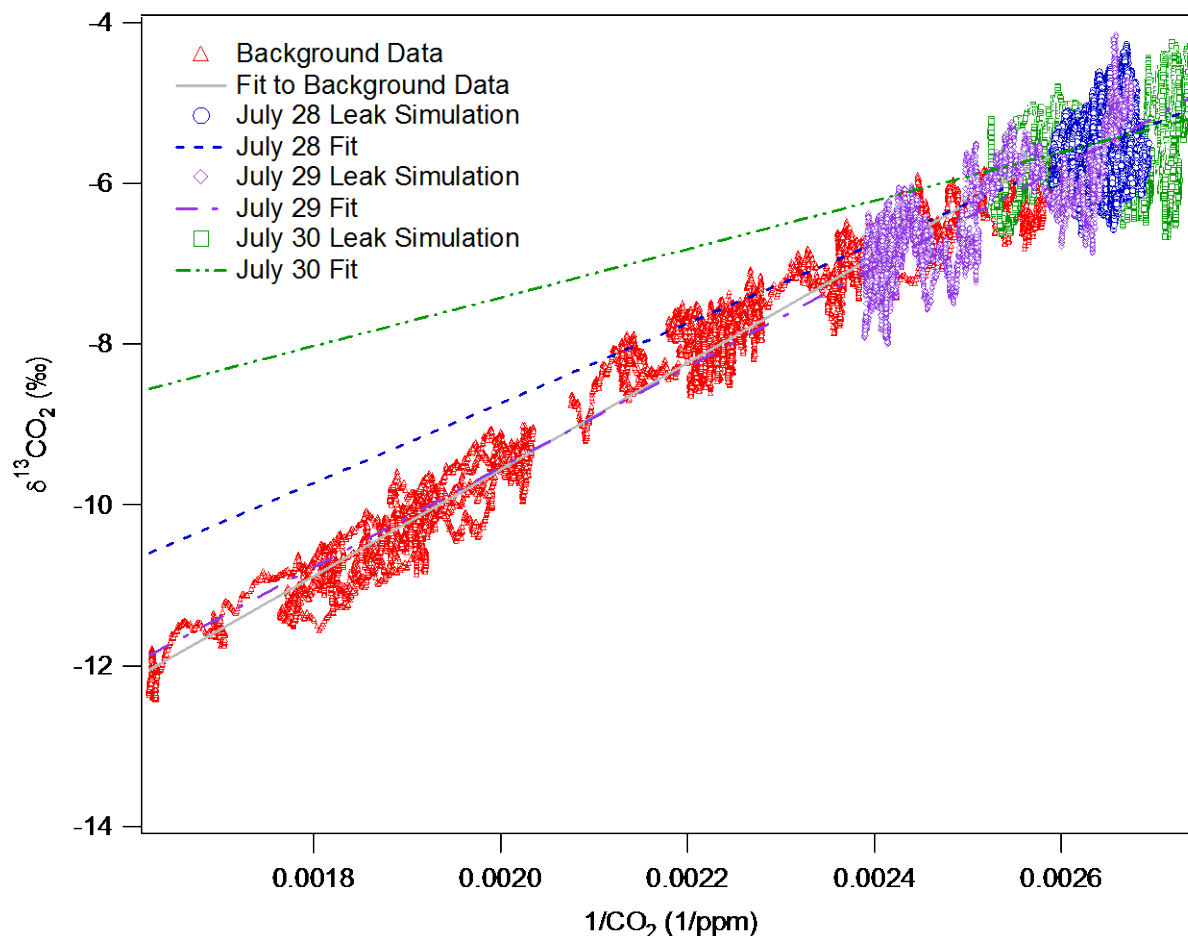
Figure 16. Model G1101-*i* Minimum Detectable Leak Rate Results for Day 3 (7/30/2010)

Table 14. Minimum Detectable Leak Rate Keeling Plot Results

	Background			Leak Test			Distinct
		95%			95%		Mixing
Test Date	**Intercept**	**CI**	**R_2**	**Intercept**	**CI**	**R^2**	**Curve**
July 28, 2010	−23.35	0.59	0.2330	−18.67	0.41	0.0594	Yes
July 29, 2010	−22.99	0.08	0.8432	−21.99	0.12	0.6427	Yes
July 30, 2010	−23.22	0.03	0.9858	−13.45	0.21	0.1184	Yes

The equivalent leak rate as a function of source $\delta^{13}C$ was also back-calculated for several relevant $\delta^{13}C$ values: −3.5‰, −20‰, and −35‰. The results of those calculations are summarized in Table 15. The predicted CO_2 concentration for the various CO_2 sources begin to show increases over the ambient concentration for the leaks of 15 LPM or greater.

Table 15. Extrapolated Minimum Detectable Leak Rate Results

CO$_2$ Source	Leak Source δ^{13}C (‰)	Total Flow Rate (LPM)	Leak Flow Rate (LPM)	Predicted CO$_2$ Concentration (ppm)	Predicted δ^{13}C (‰)
None	−6.41	1.28×10^6	0	408.6	−6.4
99.95% ^{12}CO$_2$	−955.5	1.28×10^6	0.423	409.0	−7.3
Fossil fuels	−35	1.28×10^6	14.62	421.3	−7.3
Fossil fuels	−20	1.28×10^6	31.84	436.3	−7.3
Heavy	−3.5	1.28×10^6	19818	580.7	−5.6

(a) Data in this table are reported to the number of significant digits appropriate for the respective analyzer's reported accuracy and precision.

6.9 Ambient Air Monitoring

The Model G1101-*i* was set up to monitor ambient air when not engaged in other testing activities during Phase 2 and Phase 3. For Phase 3, a meteorological station was positioned near the injection well, as shown in Figure 4; meteorological data are reported with the Model G1101-*i* ambient air CO$_2$ concentration and δ^{13}C readings in Figure 17. The ambient data set collected by the Model G1101-*i* is shown in the bottom panel for CO$_2$ concentration and δ^{13}C. The upper panels show ambient temperature, RH, wind speed, and wind direction. The average ambient CO$_2$ concentration was 411 ppm, with a range of 365 to 488 ppm. The average measured stable isotope ratio was −6.4‰ and values ranged from −9.5 to −4.3‰. The GS site experienced hot and humid conditions with light to moderate winds except during thunderstorms, which passed through the area on August 4 and August 5, 2010. The relationship between CO$_2$ concentration and δ^{13}C was investigated by producing a Keeling Plot, as shown in Figure 18. The value of the intercept, which represents the δ^{13}C of the CO$_2$ source, is −23.15‰, is consistent with the value for captured CO$_2$ at this site.
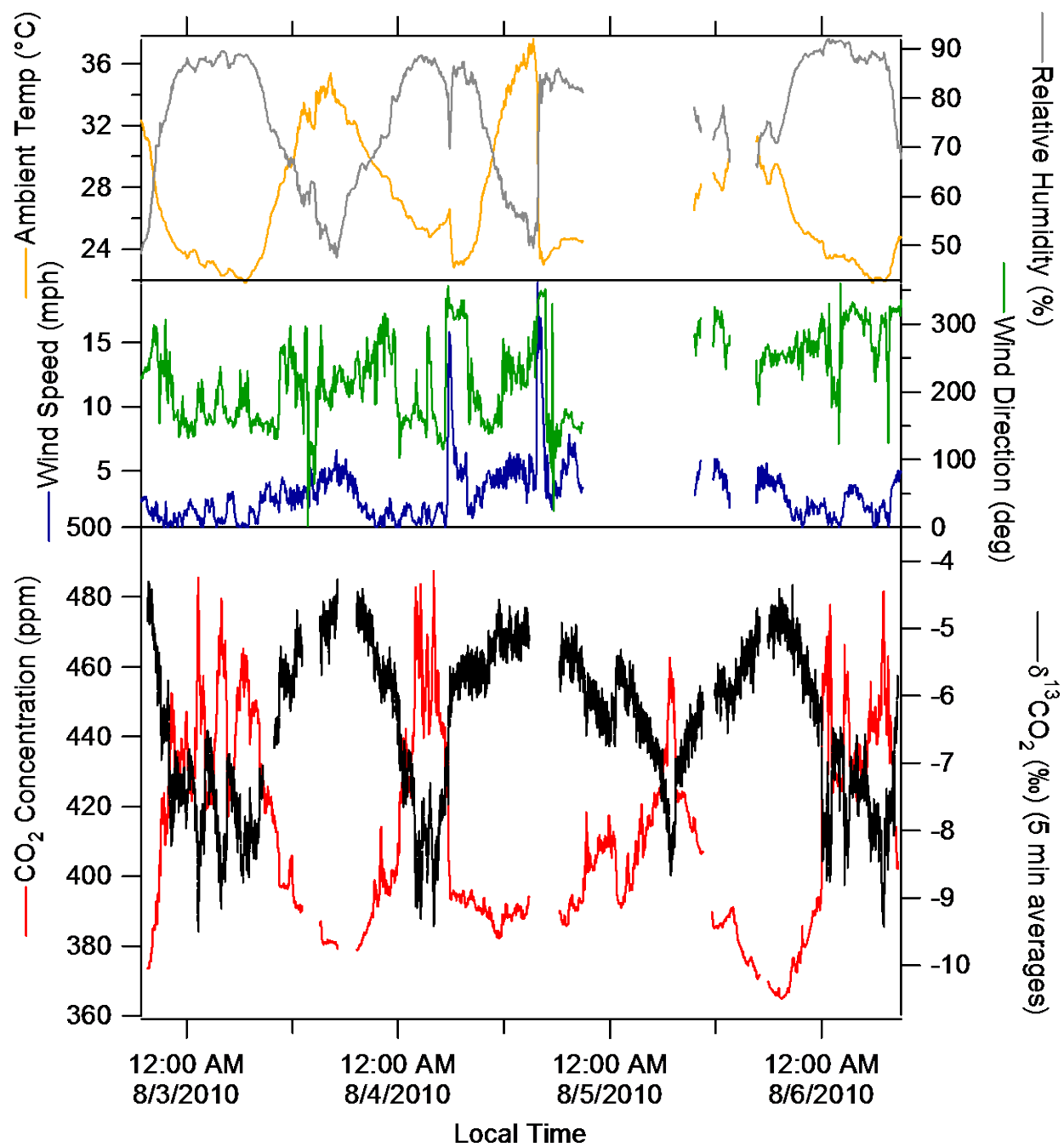
Figure 17. Meteorological Conditions and Model G1101-*i* Ambient Air CO₂ Measurements at the GS Site
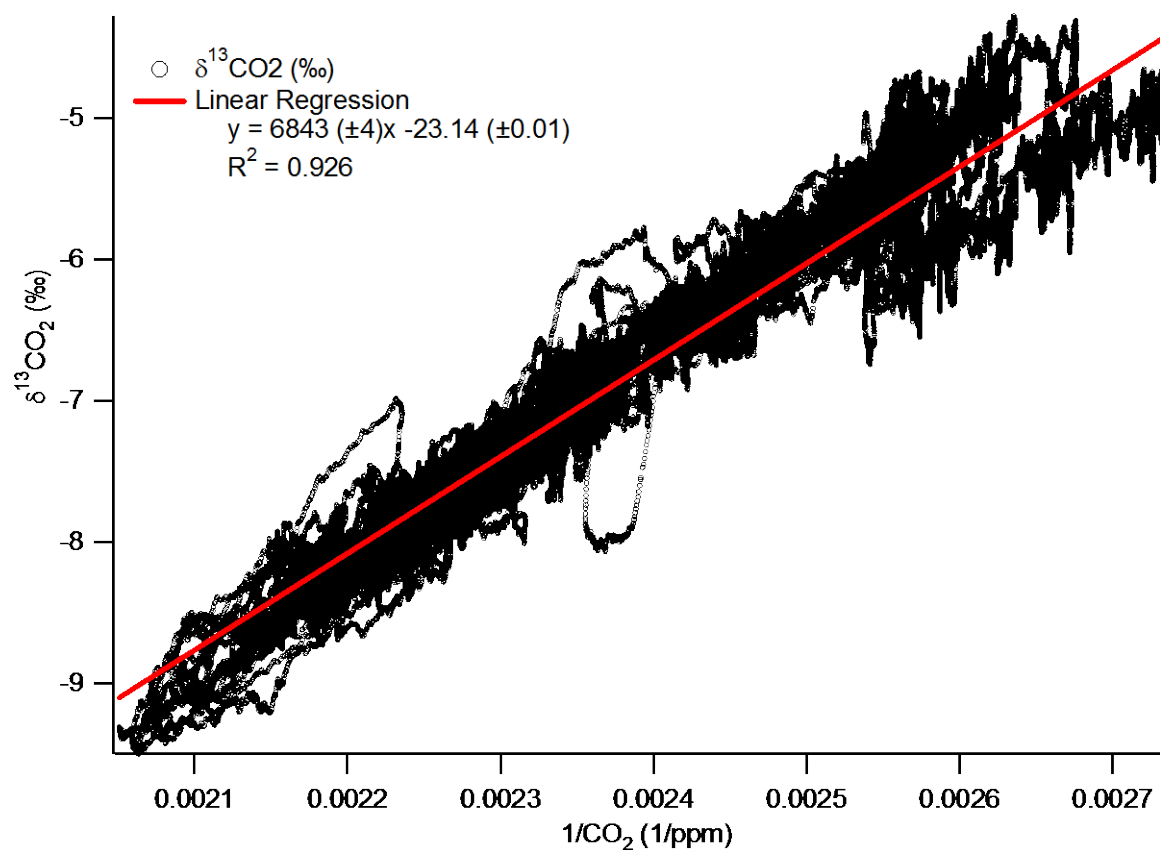
Figure 18. Keeling Plot of Model G1101-*i* Ambient Air Data

During the ambient air monitoring period, a valve near the main sequestration well was opened for approximately one minute. Prior to the intentional release of captured CO_2, the inlet to the Model G1101-*i* was positioned 0.86 m downwind of the valve. Figure 19 shows the raw data and 30-second averages for CO_2 concentration and isotope ratio data reported by the Model G1101-*i* during the release. The period during which the valve was open is shaded in gray and the points at which the leak was detected in the Model G1101-*i* data are marked by open symbols ($\bigcirc,\square,\diamondsuit$). The leak response time was determined relative to CO_2 concentration and isotope ratio, as described in Section 5.8. A change in CO_2 concentration was qualitatively identified 29 seconds after the valve was opened; the CO_2 concentration reached 1000 ppm 42 seconds after the valve was opened. A decrease in measured isotope ratio at least 2 standard deviations from the average value was observed after 39 seconds. Using all three methods, the leak was detected by the Model G1101-*i* less than 60 seconds after the leak was initiated.

A Keeling plot was generated from the data shown in Figure 19 (using 30-second averages) and a linear regression calculated for the data. Data above the regression line are from the beginning of the leak (beginning in the shaded area of the lower panel); data fell below the regression line as values returned to background levels. The R^2 value was 0.939 and the intercept was −24.0 ($\pm$ 0.2)‰, which is similar to the intercept found for ambient measurement data (Figure 17) and is consistent with the isotope ratio of the CO_2 being injected at this site.
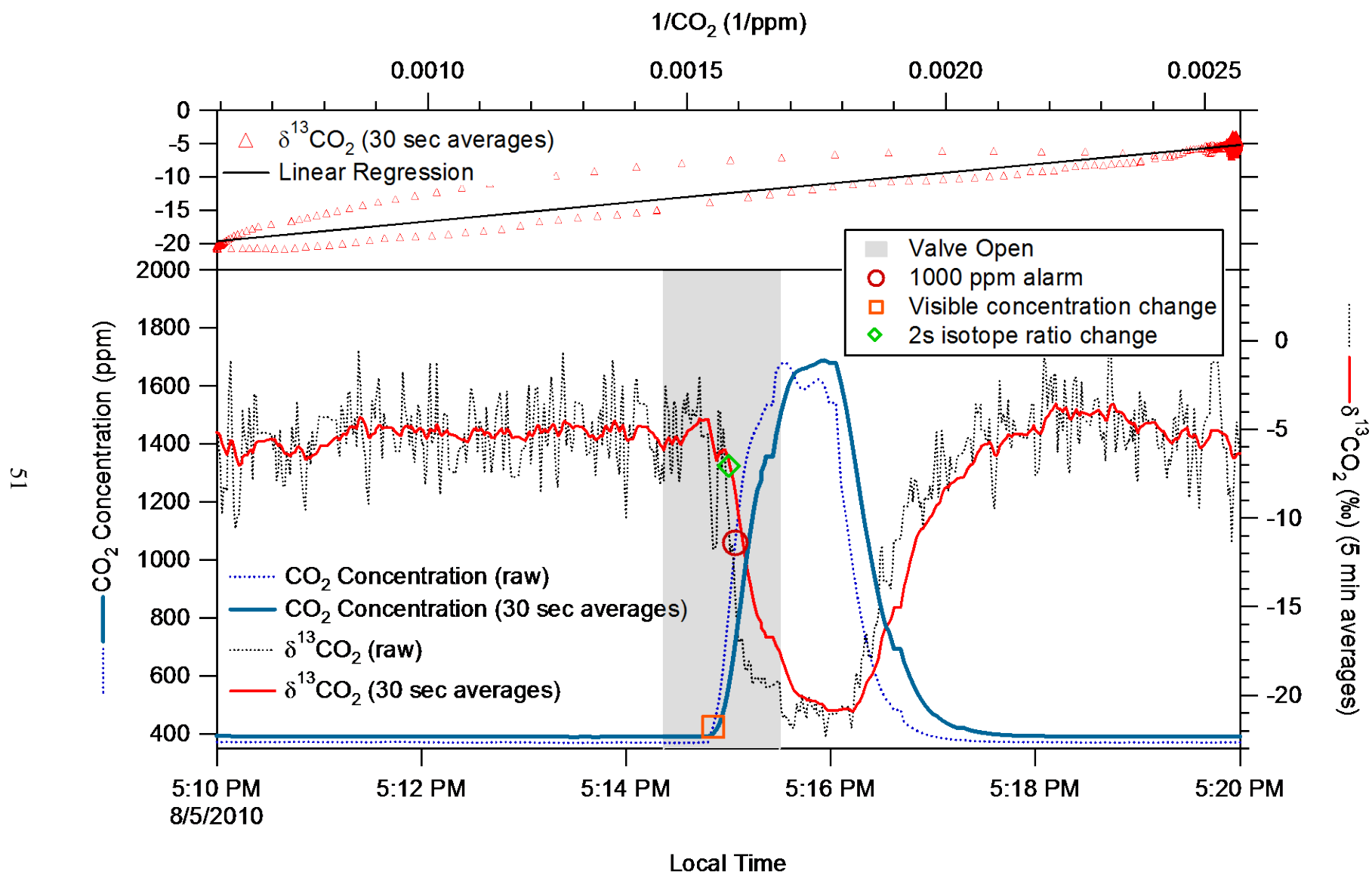
Figure 19. Leak Response Time Results

6.10 Mobile Surveys

Twice during Phase 3 the Model G1101-*i* was installed in the Nissan Altima hybrid to conduct mobile surveys as described in Chapter 3. Results from the mobile surveys have been analyzed in a qualitative manner to evaluate whether the Model G1101-*i* could reasonably be operated in mobile survey mode. Once the first installation in the vehicle had been completed, it generally took approximately 15 minutes with two testing staff to shut down the analyzer, move all components into the vehicle, and begin collecting data under battery power. Some additional time was then needed for the analyzer response to stabilize. At least one hour of monitoring data could be collected on a single battery. A summary of the features, their brief descriptions, and other identifying features is provided in Table 16.

Table 16. Mobile Survey Features and Identifiers

Survey Date	Feature Number	Identifier	Description	Environment
August 3, 2010	1		Shallow aquifer monitoring well	Near evergreen trees
	2		Shallow aquifer monitoring well	Near evergreen trees
		A	Approach by additional vehicle	
		B	No feature	Evergreen trees
	3		Deep monitoring well	Gravel lot
	4		Shallow aquifer monitoring well	Gravel lot
	5		Soil gas monitoring well	Gravel lot
	6		Soil gas monitoring well	Gravel lot
	7		Shallow aquifer monitoring well	Lagoon berm
	8		Shallow aquifer monitoring well	Roadside
	9		Shallow aquifer monitoring well	Roadside
	10		Shallow aquifer monitoring well	Roadside
August 6, 2010		M	Meteorological Station	
	11		Above-ground transmission lines	Gravel lot
	12		Injection well	Gravel lot
	13		Injection well	Gravel lot
	14		Soil gas monitoring well	Edge of gravel lot
	15		Soil gas monitoring well	Edge of gravel lot
	16		Deep monitoring well	

Figure 20 shows time series data for the Model G1101-*i* concentration and $\delta^{13}C$ response during the mobile survey conducted on August 3, 2010. The vertical black lines labeled 1 through 10 show the various features that were surveyed. The line labeled "A" shows the point where another vehicle approached the hybrid sedan during the survey and shows that exhaust from the other vehicle was sampled by the Model G1101-*i*. Water vapor concentration data measured by the Model G1101-*i* are included in the top panel (red trace) to assist in identification of vehicle exhaust, which is expected to have increased water vapor. Features 1 and 2 were surrounded by

evergreen trees; at point "B," the vehicle approached trees without a well feature as a comparison. The vehicle slowed dramatically or came to a complete stop at each of the features and some were sampled twice. Figure 21 shows the GPS for the surveys of Features 1 and 2 that have been colored according to the Model G1101-i $\delta^{13}C$ value at each point. The impact of the second vehicle is apparent around point A in Figure 21. Other spikes in the CO_2 concentration and isotope ratio, for example between Features 3 and 4, appeared to be caused by the Nissan Altima emissions when in non-electric vehicle mode.

Data from the second set of mobile surveys are shown in Figure 22 and Figure 23. Each feature was passed twice. During this survey, the vehicle was driven out to the plant to charge the battery before and during the survey. The location of the meteorological station is marked as "M" in Figure 22. On the second approach to Feature 16, the hybrid sedan exited electric vehicle mode; it is likely that emissions from the vehicle were being sampled at that time. Water vapor measurements during this survey showed very little variability and were not helpful in identifying vehicle exhaust.
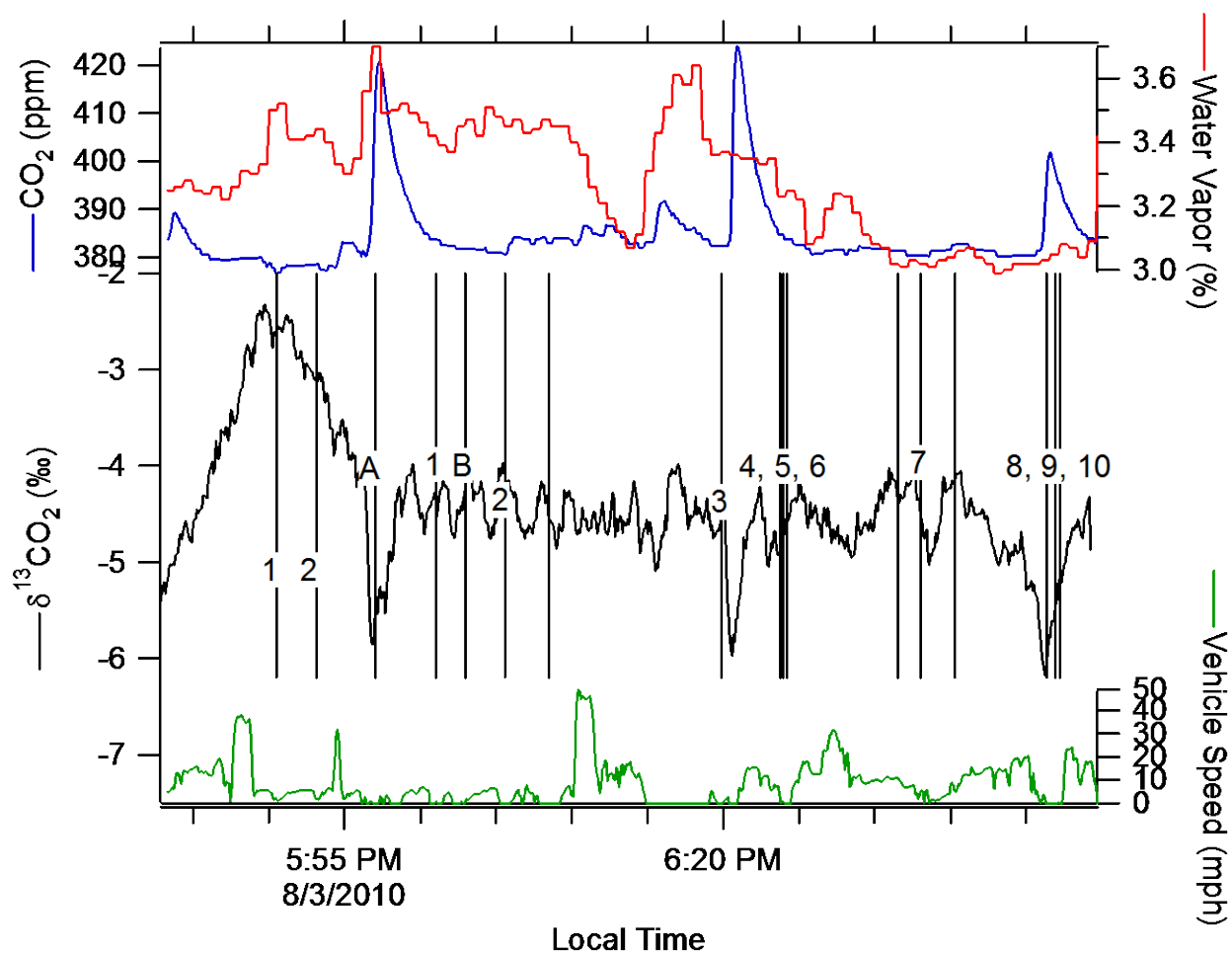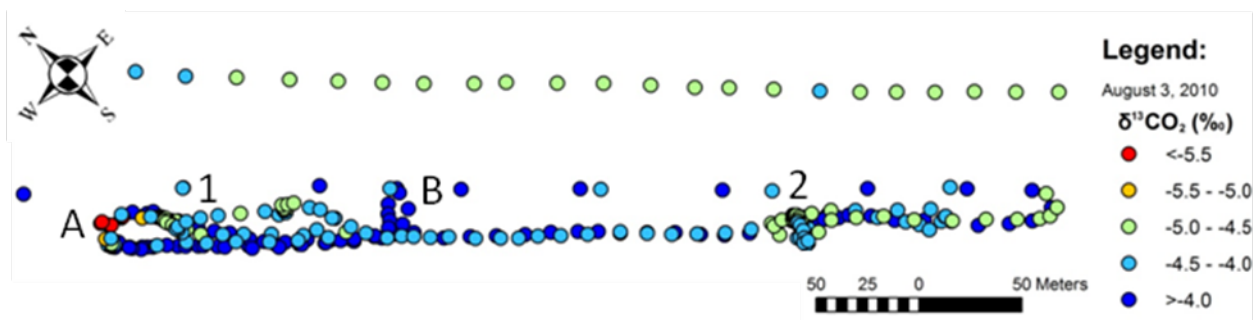
Figure 20. Mobile Survey Results

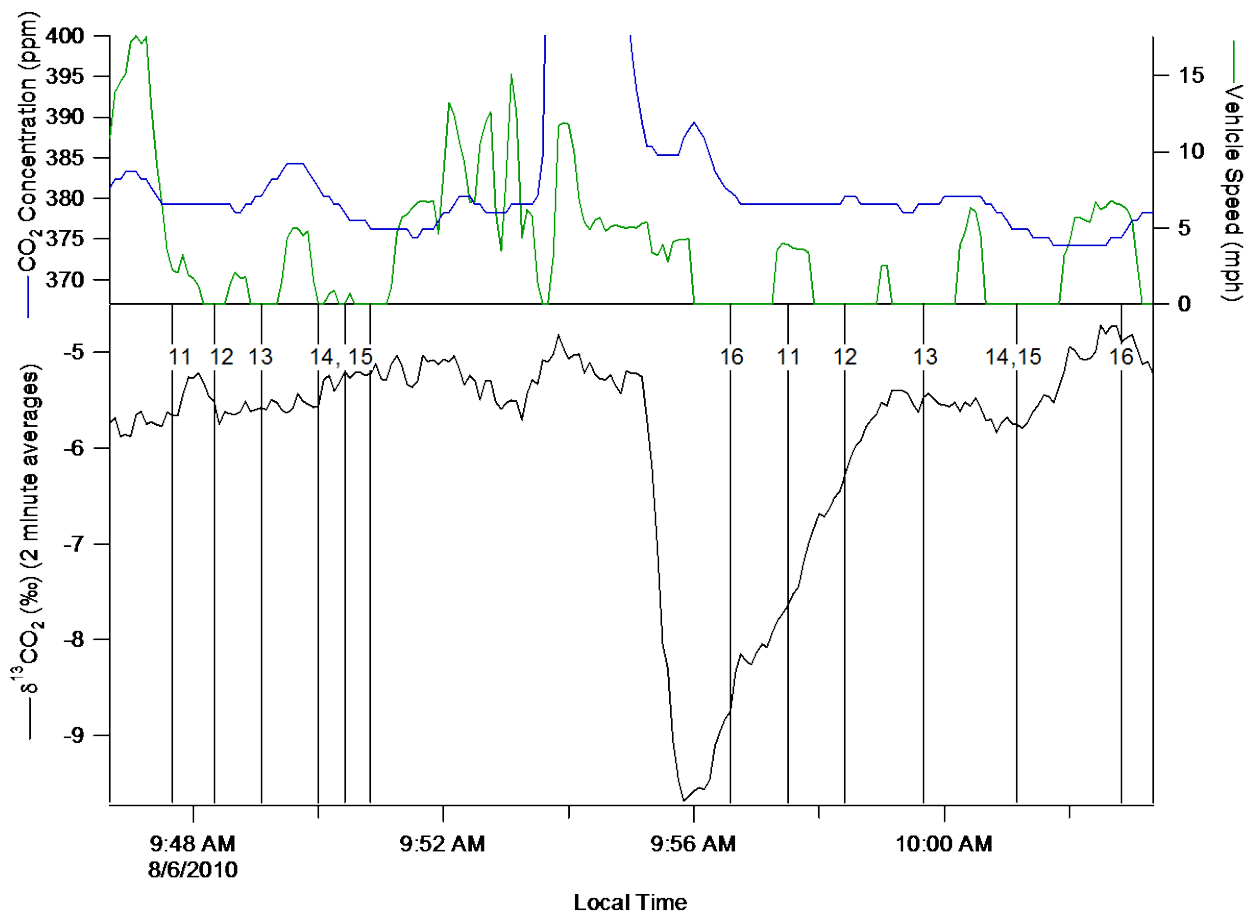**Figure 21. Mobile Survey GPS Trace of Selected Features**

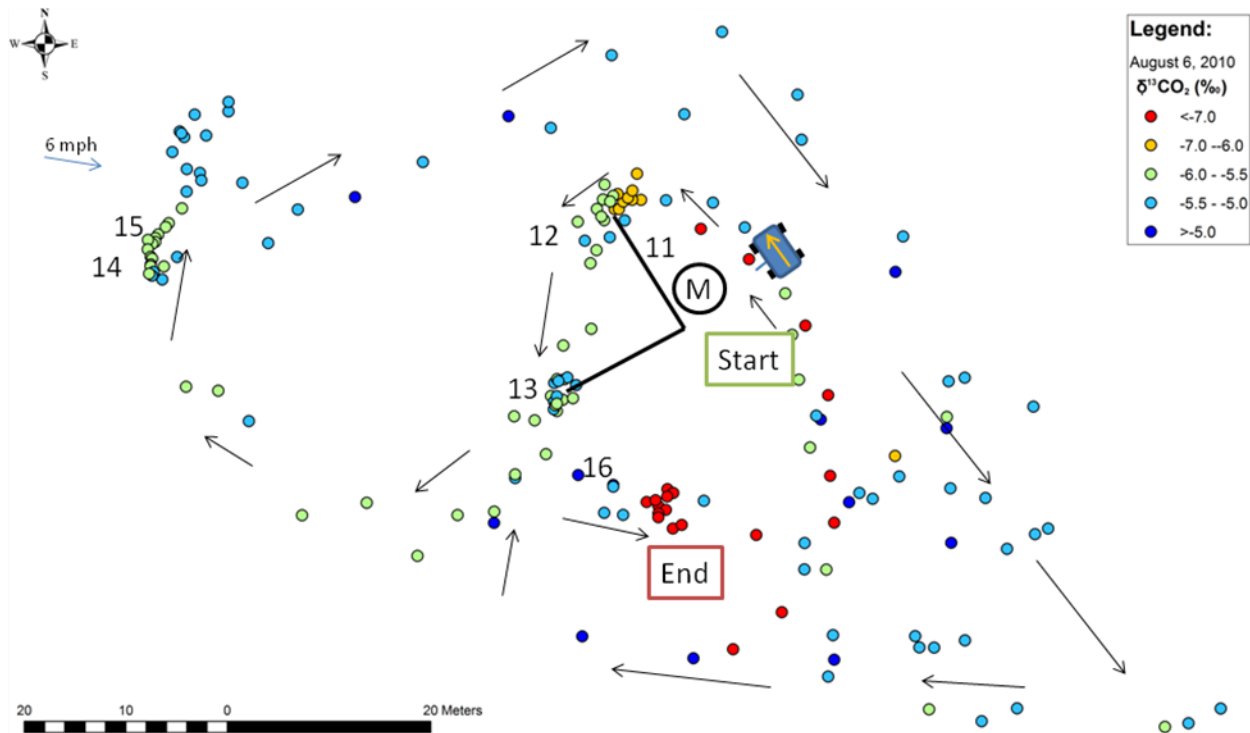**Figure 22. Mobile Survey Results**

Figure 23. Mobile Survey GPS Trace of Features Shown in Figure 22

6.11 Reference Method Comparability

The results of 10 pairs of duplicate ambient air reference method measurements were compared to the average Model G1101-*i* response over the five minutes preceding the sample pressurization period to determine the reference method comparability. Two sample pairs were collected during Phase 2 in the ABT with the blowers running and 8 pairs were collected during Phase 3 while the Model G1101-*i* was monitoring ambient air near the injection well. The inlet for the ambient air sampling system was collocated with the Model G1101-*i* inlet and the sampler positioned downwind of the inlet while collecting samples. Care was taken to follow the sampling and handling instructions provided by the reference laboratory. The reference method measurements were compared to the Model G1101-*i* response by calculating the accuracy and bias for both CO_2 concentration and $\delta^{13}C$ and the results summarized in Table 17. The average accuracy for CO_2 concentration was 97.9% with a range of 93.8% to 100.5%. For $\delta^{13}C$, the average difference was −3.0‰ and values ranged from −3.5‰ to −2.1‰. Bias was calculated separately for each site. At the ABT and GS site, concentration bias was −0.2% and −2.5%, respectively.

Table 17. Reference Method Comparability Results

	Date (2010)	Site	Time	CO$_2$ Concentration Reference Method (ppm)	Model G1101-*i* (ppm)	%R	CO$_2$ δ^{13}C (‰) Reference Method	Model G1101-*i*	Difference
1	7/29		16:55	372.24[a]	368.7	99.0	−7.653	−4.8	−2.9
2	7/29	ABT	16:55	372.22	368.7	99.0	−7.597	−4.8	−2.8
3	7/30		10:11	391.81	393.6	100.4	−8.133	−6.1	−2.1
4	7/30		10:11	391.51	393.6	100.5	−8.139	−6.1	−2.1
5	8/3		10:54	402.72	397.0	98.6	−8.625	−5.8	−2.9
6	8/3		10:54	402.51	397.0	98.6	−8.636	−5.8	−2.9
7	8/4		10:34	395.10	388.2	98.3	−8.412	−5.4	−3.0
8	8/4		10:34	395.04	388.2	98.3	−8.447	−5.4	−3.0
9	8/4		12:34	394.52	389.0	98.6	−8.462	−5.1	−3.4
10	8/4		12:34	394.66	389.0	98.6	−8.439	−5.1	−3.4
11	8/4		13:36	395.55	391.2	98.9	−8.543	−5.0	−3.5
12	8/4	GS	13:36	395.16	391.2	99.0	−8.471	−5.0	−3.5
13	8/5		10:05	413.87	408.8	98.8	−9.272	−6.1	−3.2
14	8/5		10:05	414.04	408.8	98.7	−9.324	−6.1	−3.2
15	8/5		16:03	401.69	376.7	93.8	−8.715	−5.8	−2.9
16	8/5		16:03	401.84	376.7	93.8	−8.715	−5.8	−2.9
17	8/5		16:44	395.45	371.1	93.8	−8.438	−4.9	−3.5
18	8/5		16:44	395.09	371.1	93.9	−8.472	−4.9	−3.5
19	8/6		8:32	415.71	412.6	99.2	−9.411	−6.7	−2.7
20	8/6		8:32	417.66	412.6	98.8	−9.455	−6.7	−2.8
Average						97.9%			−3.0
Minimum						100.5%			−2.1
Maximum						93.8%			−3.5
Bias (%D)	ABT					−0.2%			
	GS					−2.5%			

(a) Data in this table are reported to the number of significant digits appropriate for the analyzer's reported accuracy and precision.

6.12 Data Completeness

The Model G1101-*i* operated for 100% of the available time during Phase 1 and Phase 2 of the verification test. During Phase 3, internal calibrations took place during 7% of the available testing time (6 hours). The calibrations were initiated after the analyzer had been powered by a deep cycle marine battery that was not sufficiently charged to power the analyzer. Due to the behavior of the inverter, power to the Model G1101-*i* cycled on and off every few minutes for approximately 30 minutes. Inspection of the log files by the vendor revealed that an internal error occurred during that period and this triggered the internal calibrations at the next startup. Upon completion of the internal calibrations, the analyzer resumed measurements. When supplied with the necessary power (i.e., a fully charged battery), the Model G1101-*i* data return during mobile survey testing was 100%. During a period of 2.6 hours, the temperature in the

shed at the GS site exceeded the operating limits identified by the vendor and testing staff elected to power off the analyzer until an air conditioner could be installed in the shed. The internal calibrations and temperature-related downtime resulted in a 91% data return during Phase 3 of this verification test.

6.13 Operational Factors

The Model G1101-*i* was installed in the laboratory and at both field sites by Battelle testing staff; the installation was completed in less than one hour. The vendor was readily available to answer questions and provide support, but no formal training was provided on the instrument. Instructions in the user manual for the installation were clear and easy to follow. A checklist was provided by the vendor representative to establish whether the analyzer was in proper working order during the test. The checklist, shown in Appendix A, was completed by Battelle staff during the daily checks of the Model G1101-*i* operating status. No maintenance was performed on the analyzer. Data were downloaded on a daily basis to a USB memory stick or expansion drive. The Model G1101-*i* did not generate any waste or use consumable supplies. Batteries used to operate the Model 1101-*i* during Mobile Surveys were reusable and rechargeable.

In general, the Model G1101-*i* software was easy to use. Battelle staff found the zoom and other features on the graphical display to be somewhat cumbersome and not especially intuitive. Ease of use of the software improved with practice.

Chapter 7
Performance Summary

The performance of the Picarro Model G1101-*i* was evaluated for its accuracy, bias, precision, linearity, response time, and temperature/RH bias by evaluating the Model G1101-*i* response while sampling dilutions of known concentration from certified CO_2 gas standards and ambient air. When possible, performance parameters were calculated for the Model G1101-*i* CO_2 concentration and $\delta^{13}C$ response. The ability of the Model G1101-*i* to detect CO_2 leaks was evaluated under the simulated field conditions of the ABT by releasing varying amounts of pure $^{12}CO_2$ into ambient air stream. Use of the Model G1101-*i* to conduct mobile surveys was evaluated by operating the analyzer in a hybrid vehicle and transporting it to road-accessible features at the GS site, such as CO_2 transmission lines and monitoring wells. The Model G1101−*i* was operated with the factory calibration. All gas standard dilutions were prepared using the same calibrated dynamic dilution system. Given the uncertainty estimate for the nominal CO_2 concentrations of ±7%, it is not possible to determine from these measurements alone whether the observed inaccuracies and biases are due to errors in the instrument response or the gas preparation. The results of this evaluation are described below.

Concentration Accuracy, Bias, Precision, and Response Time
The accuracy of the Model G1101-*i* was assessed over the range of 100 ppm to 5,000 ppm in terms of %R, which ranged from 90.0 to 113.1%, with an average of 96.0%. Bias, or the average percent difference between the Model G1101-*i* response and the known value, was −3.98%. Precision of the Model G1101-*i* was determined from the average responses to triplicate challenges at each of 11 CO_2 concentrations. The relative standard deviation values ranged from 0.1% to 1.2%, with an average of 0.3%. The average 95% response time was 2.43 minutes (142 seconds) for rise time and 2.53 minutes (152 seconds) for fall time. It is not possible to determine from these measurements alone whether the observed response time is limited by the response of the gas dilution system.

Concentration Linearity
Linearity was evaluated in terms of slope, intercept, and R^2. Over the 0 to 400 ppm range, the slope of the regression line was 0.935 (±0.036), with an intercept of 11.3 (±8.9) and R^2 value of 0.9958. Over 0 to 5,000 ppm, the slope of the regression line was 0.938 (±0.006), with an intercept of −1.32 (±13.6) and R^2 value of 0.9997. (The 95% confidence interval for the slope and the intercept of each line is shown in parenthesis).

Isotope Ratio Accuracy, Bias, and Linearity

The accuracy of the Model G1101-*i* δ^{13}C response was assessed at −3.60‰, −10.41‰, and −40.80‰ at three concentration levels: 259 ppm, 370 ppm, and 740 ppm. Values for δ^{13}C differed from the expected value by between 1.1 to 2.7‰, with an average of 1.7‰. The lowest absolute differences were observed for the −40.80‰ standard and at the higher CO_2 concentrations. Isotope ratio linearity was assessed in terms of slope, intercept, and R^2 for the full dataset. The slope, including all isotope ratios and concentrations, was 1.01 (±0.02) with an intercept of 1.88 (±0.37) and an R^2 value of 0.9992. (The 95% confidence interval for the slope and the intercept of each line is shown in parenthesis.) The strongest correlation between concentration and measured isotope ratio, which was evaluated at −3.60‰, −10.41‰, and −40.80‰, was observed for the −3.60‰ standard, with an R^2 value of 0.9468, a slope of −0.0025 and intercept of 3.24.

Temperature and Relative Humidity Bias

Temperature and RH bias were assessed by comparing the Model G1101-*i* CO_2 concentration and δ^{13}C response to dilutions from a certified CO_2 standard at 5 temperature/RH conditions to its response at 20°C and 0% RH. During this evaluation, the Model G1101-*i* was installed in a temperature/RH-controlled chamber; humidified zero air was added to the CO_2 gas standard dilution to achieve the desired RH. The following test conditions were evaluated: 20°C/50% RH; 20°C/90% RH; 32°C/50% RH; 32°C/90% RH; 4°C/50% RH. In general, variability in ambient temperature and RH conditions resulted in bias values of 3% or less for the Model G1101-*i* concentration measurements and 0.7‰ or less for isotope ratio. The maximum concentration bias value, 3.0%, was observed for CO_2 concentration at 4°C/50% RH. The largest isotope ratio average difference of 0.7‰ was observed for 32°C/90% RH.

Minimum Detectable Leak Rate

The ability of the Model G1101-*i* to identify CO_2 leaks above ambient air variability was evaluated by simulating leaks under controlled field conditions in the Ambient Breeze Tunnel. Pure $^{12}CO_2$ was periodically released into a constant flow of ambient air and the flow rate adjusted until the Model G1101-*i* difference in the δ^{13}C response during the "leak" compared to ambient air was greater than 2 times the ambient air δ^{13}C variability. Under conditions that simulated 1.8 m/s winds, the minimum detectable leak rate was 0.423 LPM $^{12}CO_2$, which resulted in a 0.9‰ decrease, on average, in the Model G1101-*i* δ^{13}C readings compared to ambient air (approximately −6.4‰). This result was extrapolated to determine the equivalent leak rates for CO_2 sources of with δ^{13}C values −35‰, −20‰, and −3.5‰. The equivalent leak rates were 14.62 LPM, 31.84 LPM, and 198.18 LPM, respectively.

Ambient Air Monitoring

The Model G1101-*i* monitored ambient air at the GS site between August 2 and August 6, 2010. During this period, the average ambient CO_2 concentration was 411 ppm, with a range of 365 to 488 ppm. The average measured stable isotope ratio was −6.42‰ and values ranged from −9.50 to −4.28‰. The relationship between CO_2 concentration and δ^{13}C was investigated by producing a Keeling Plot. The value of the intercept, which represents the δ^{13}C of the CO_2 source, is −23.1‰ and is consistent with the value for captured CO_2 at this site. An intentional release of captured CO_2 was detected by the Model G1101-*i* in less than 60 seconds. A Keeling Plot of the data from the intentional release period had an R_2 value of 0.939 and an intercept of

−24.0 (± 0.2)‰, which is similar to the intercept found for ambient measurement data and is consistent with the isotope ratio of the CO_2 being injected at this site.

Mobile Surveys
During Phase 3, the Model G1101-*i* was transported to road-accessible features of the GS, such as transmission lines and monitoring wells, to evaluate the ease of use and operational factors of the analyzers during use in a mobile survey mode. The Model G1101-*i* surveyed 16 features at the GS while installed in the back seat of a Nissan Altima hybrid sedan and operating on power from a marine deep cycle/RV battery and power inverter. Once the first installation in the vehicle had been completed, it generally took approximately 15 minutes with two testing staff to shut down the analyzer, move all the components into the vehicle, and begin collecting data under battery power. Some additional time was then needed for the analyzer response to stabilize. At least one hour of monitoring data could be collected on a single battery.

Comparability to Reference Methods
Comparability was determined as the accuracy (%R) and bias (average percent difference) of the Model G1101-*i* response compared to CO_2 concentration (NDIR) and $\delta^{13}C$ (IRMS) reference method results for 10 duplicate grab samples of ambient air. The average accuracy for CO_2 concentration was 97.9% with a range of 93.8% to 100.5%. For $\delta^{13}C$, the average difference was −3.0‰ and values ranged from −3.5‰ to −2.1‰. Bias was calculated separately for each site. At the ABT and GS site, concentration bias was −0.2% and −2.5%, respectively.

Data Completeness
The Model G1101-*i* operated for 100% of the available time during Phase 1 and Phase 2 of the verification test. During Phase 3, internal calibrations took place during 7% of the available testing time (6 hours) and the analyzer was shut down for 2.6 hours because ambient temperatures in the shed where the analyzer was operated exceeded operating limits identified by the vendor. The internal calibrations and temperature-related downtime resulted in a 91% data return during Phase 3 of this verification test.

Operational Factors
The Model G1101-*i* was installed in the laboratory and at both field sites by Battelle testing staff; the installation was completed in less than one hour; no formal training by the vendor was necessary. Instructions in the user manual for the installation were clear and easy to follow. A checklist was provided by the vendor representative to establish whether the analyzer was in proper working order during the test. No maintenance was performed on the analyzer. Data were downloaded on a daily basis to a USB memory stick or expansion drive. The Model G1101-*i* did not generate any waste or use consumable supplies. In general, the Model G1101-*i* software was easy to use. Battelle staff found the zoom and other features on the graphical display to be somewhat cumbersome and not especially intuitive. Ease of use of the software improved with practice.

Vendor-Supplied Specifications
The Model G1101-*i* weighs 26.3 kg (58 lbs), has dimensions of $43 \times 25 \times 59$ cm ($17" \times 9.75" \times 23"$) including the feet, and can be rack mounted or operated on a bench top. The approximate purchase price of the Model G1101-i is US $60,500.

Chapter 8
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Appendix A
Daily Checklist

DAILY CHECKLIST
Picarro G1101-*i* Analyzer for Isotopic CO₂
ETV Verification Test of Isotopic Carbon Dioxide Analyzers
for Carbon Sequestration Monitoring

Instrument Performance:

☐ Check the 'status' window (scroll up to see all messages) and record any messages:

_____

  o Contact vendor for any questions about warnings. Vendor contact:

  Chris Rella   **408.962.3941**
  Picarro, Inc.   **rella@picarro.com**

☐ Put the GUI into 'service mode'. Service mode is identified by an 's' in the LED in the upper right. To select service mode, go to Settings/Change GUI mode, and then type the password 'picarro' (no quotes) and click ok.

  o Verify that the following sensors are within normal operating parameters, by selecting the appropriate item from the dropdown list and recording the min / max data from the graph.

Actual Value	Parameter	Normal Range	Within Range? (Y/N)
	CAVITY_TEMP	45°C ± 0.02°C	
	WB_TEMP	45°C ± 0.02°C	
	CAVITY_PRESSURE	140 Torr ± 0.2 Torr	
	DAS_TEMP	10 - 40 °C (this is an indication of the ambient temperature)	

These same activities can be performed by analyzing the xxx_data.dat files, found in the C:\Userdata\YYYYMMDD directory structure (see below). These values (along with many more diagnostic values) can be found in a simple space-delimited ASCII data file.

☐ Record instrument flow rate with a calibrated flow meter. (Value should be ~20 sccm)

Flow meter SN:_____   Flow rate: _____

Daily Data backup:

☐ Standard Data files: User data is available in C:\UserData\YYYYMMDD. Download (copy) all .dat files from the daily directories into a flash drive or via an ethernet connection.

☐ Spectral data: All raw spectral data are located in C:\Picarro\Archive\YY\MM\DD\HH directories (these dates in times are in universal time, not in instrument local time). Download (copy) all the .zip files collected in these directory structures every day. IMPORTANT: the instrument saves only about 3-4 days of raw spectral data in a first-in first-out buffer in the archive. Be sure to download these files daily, or the information will be lost.

Operator Name: _____   Date:_____

Operator Signature:_____

Comments: _____

_____